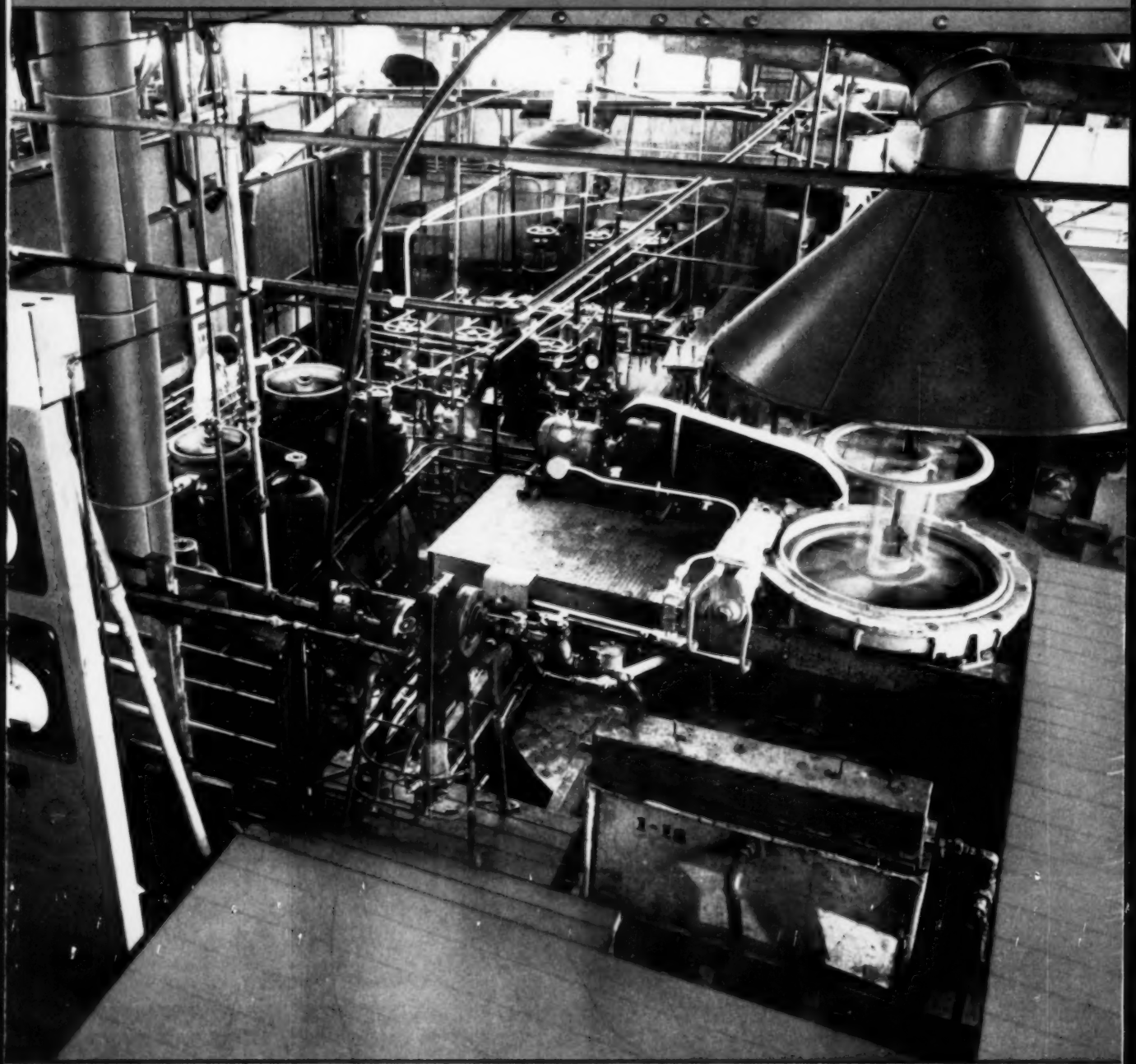
JUNE, 1953

Journal of METALS



June JOURNAL OF METALS Highlights:

"Hydrometallurgical Process Yields Pure Metal Powders From Sulphides" - p. 786
"The Reduction-Oxidation Process For The Treatment of Taconites" - p. 780
"Howe Memorial Lecture" - p. 797

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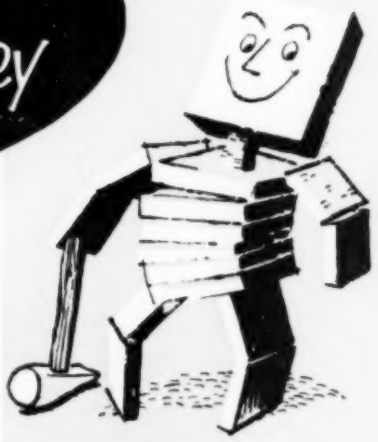

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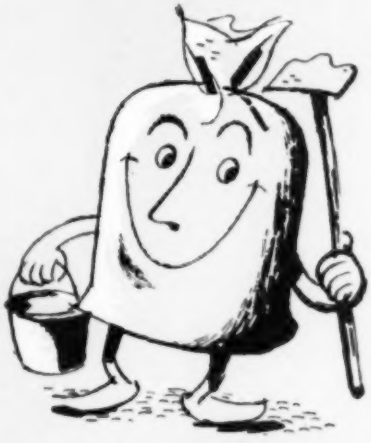

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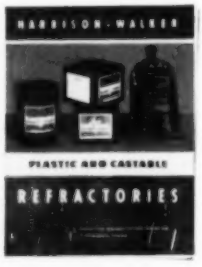

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COVER

Sherritt Gordon Mines Ltd., developed and scaled-up its hydrometallurgical method for metal recovery from nickel-copper-cobalt concentrate in a series of pilot plants. Research is continuing at the fourth pilot plant at Ottawa, while the refinery is under construction at Fort Saskatchewan, Alberta. See the story starting on p. 775.

NEWS

Meet the Authors	750	Trends	768
Employment Service	754	Drift of Things	771
New Products	757	Journal of Metals Reporter	773
Books for Engineers	761	AIME News	845
Industrial Notes	764	Coming Events	852

TECHNICAL FEATURES

Hydrometallurgical Process Yields Pure Metal Powders From Sulphides 775

Reduction-Oxidation Process for the Treatment of Taconites
F. M. Stephens, Jr., Benny Langston, A. C. Richardson 780

Mechanization Program Results in Savings at Laredo Antimony Smelter
R. L. Kulpaca, J. C. Archibald, Jr. 786

Chihuahua Slag Fuming Plant to Process 19,000 Tons per Month
V. R. MacDonald 789

Lorain Cuts Banked Blast Furnace Blowing-In Time from 72 to 30 Hours
W. W. Durfee 791

Steam Jets Efficiently Remove Dust from Open Hearth Furnace Flues
John Peterson 794

Open Hearth Screw Steels Replacing Bessemer S. Feigenbaum 796

TRANSACTIONS

Influence of the Rate of Deformation on the Tensile Properties of Some Plain Carbon Sheet Steels Joseph Winlock 797

Vapor Pressure of Zinc in the Reduction of ZnS by Cu and Fe
A. W. Bethune, L. M. Pidgeon 804

Recrystallization and Stored Energy H. P. Leighly, H. L. Walker, J. W. Marx 809

Magnetic Annealing of a Co-Fe Alloy
A. H. Geisler, J. P. Martin, E. Bath, J. H. Crede 813

Order-Disorder Transformation in Cu-Au Alloys Near the Composition CuAu
J. B. Newkirk 823

Self-Diffusion of Iron in Iron Oxides and the Wagner Theory of Oxidation
L. Himmel, R. F. Mehl, C. E. Birchenall 827

TECHNICAL NOTES

Kinetics of Galvanizing D. J. Blickwede 807

Concentration Gradients Associated with Growing Pearlite R. E. Grace 820

Importance of the Iron Content of High-Purity Aluminum M. Metzger, J. Intrater 821

High Temperature Corrosion in Nickel-Chromium Alloys
Norman Spooner, J. M. Thomas, L. Thomassen 844

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Meet The Authors

Joseph Winlock (p. 797), 1953 Howe Memorial Lecturer, is presently chief metallurgist for the Budd Co., Philadelphia. Mr. Winlock was born in Cambridge, Mass., and attended Harvard University, (A.B., 1915). After graduation he was employed by the Lackawanna Steel Co., Buffalo. In March 1917 he enlisted in the Navy for the duration of World War I. He became a lieutenant (j.g.) and in 1919 returned to the Harvard Engineering School. He was then an assistant metallurgist in the Bureau of Mines and did research work for the National Research Council. After two years with the Watertown Arsenal as chief metallographer, he joined the Budd Co. in 1922. Mr. Winlock received the Howe Medal of the ASM with Dr. Ralph Leiter, in 1938. During the time of his employment by the Budd Co., Mr. Winlock has been abroad to England, France, and Germany. He is a member of the AIME Philadelphia Section, ASM, ASTM, British Iron and Steel Institute, and various other professional societies.

JOSEPH WINLOCK

BENNY LANGSTON

Benny Langston (p. 780), one of the co-winners of the JOURNAL OF METALS Award given at the Blast Furnace, Coke Oven and Raw Materials Conference, has been a research engineer at Battelle Memorial Institute since 1948. Born in Tuscaloosa, Mr. Langston graduated from the University of Alabama (B.S.) in 1948. When he isn't shooting pictures with his movie camera, Mr. Langston enjoys a few rounds of golf.

Frank Arthur Forward (p. 775), professor and head of the dept. of mining and metallurgy, University of British Columbia, furnished the data for the article on p. 775. Prof. Forward was born at Ottawa and attended the Ottawa Collegiate Institute and University of Toronto. He has been on the staff of the University of British Columbia since 1935. Prof. Forward had several patents granted and others are pending. He holds membership in various societies both in the U. S. and Canada, and has had many papers published.

Lawrence Himmel (p. 827) is a graduate of Cornell University presently employed by the Westinghouse Electric Corp. Born in Toronto, Canada, Mr. Himmel had worked on the Manhattan Project in New York and Oak Ridge. In 1951 he joined the research laboratories of Westinghouse as a research engineer.

LAWRENCE HIMMEL

J. P. MARTIN

J. P. Martin (p. 813) was born in Salt Lake City. A graduate of the University of Utah, he received his B.S. in 1943. Since 1946 Mr. Martin has been research metallurgist for the Allegheny Ludlum Steel Corp. During his career, Mr. Martin has been a hard rock miner with U. S. Smelting, Refining & Mining Co.; engineering aide with the Bureau of Mines; and was a lieutenant with the Navy Bureau of Ordnance. In his free time Mr. Martin does some fishing and is interested in politics.

R. L. Kulpaca (p. 786) is a Westerner, having been born in Lead, S. D. Mr. Kulpaca was in the service from 1944 to 1946 when he returned to school. He holds a B.S. degree from the South Dakota School of Mines and Technology. For approximately two years he was employed as a chemist by the International Smelting & Refining Co., Tooele, Utah. In 1949 he joined the Texas mining & smelting div., National Lead Co., Laredo, Texas as metallurgist. In 1951 he was promoted to plant superintendent, a position he presently holds. A member of the Metals Branch of AIME, Mr. Kulpaca counts music, fishing, and swimming as his hobbies.

D. J. Blickwede (p. 807) is an AIME member who does water color painting in his spare time. He also enjoys gardening when time permits. Born in Detroit, he is a graduate of Wayne University, Stevens Institute of Technology, and Massachusetts Institute of Technology. From 1943 to 1945 Mr. Blickwede was metallurgist with the Curtiss Wright Propeller Div. He was section head Naval Research Laboratory and then joined the Bethlehem Steel Co., where he is presently research engineer.

J. C. Archibald, Jr. (p. 786) has had experience in mining and milling, and cyanidation and flotation. He was born at San Luis Potosi, Mexico and graduated from the Montana School of Mines. Prior to working for the government at the Metal Reserves Co. in Brazil, he had been general superintendent for the Monongahela-Mt. Washington Mining Co., Wickes, Mont. He subsequently worked for the FEA in Washington, D. C. In 1946 he undertook exploration work in Sonora and Arizona. Mr. Archibald became unit superintendent for National Lead Co. at the Cia. Minera y Refinadora Mexicana, S.A. At the time of his transfer to the United States he held the position of general superintendent for all of the Mexican antimony mining operations for National Lead through its subsidiaries. In July 1953 he was appointed manager of the Texas mining & smelting div.

Eberhard Both (p. 813), physicist with the Signal Corps Engineering Laboratory, Fort Monmouth, was born at Ahrweiler, Germany. Dr. Both received his Ph.D. from the University of Bonn. From 1935 to 1947 he was associated with Vacuumschmelze A. G., Hanau, Germany. In 1943 he was named director of research, a position he held until 1947. Since 1947 he has been a consultant to the Signal Corps specializing in magnetic materials. Now residing at Asbury Park, N. J., Dr. Both enjoys photography.

EBERHARD BOTH

J. B. NEWKIRK

J. B. Newkirk (p. 823) enjoys among his varied hobbies skiing, motorcycling, photography and swimming. Dr. Newkirk holds degrees from Rensselaer Polytechnic Institute, and Carnegie Institute of Technology. After graduation from RPI he was on the Bethlehem Steel Co. loop course. He joined the Navy and was in the South Pacific for two years during the war. After his discharge he went to Carnegie and was then a Fulbright research fellow at the Cavendish Laboratory, Cambridge, England. Upon his return he joined the research staff at General Electric Co., Schenectady. He previously coauthored two papers.

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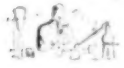

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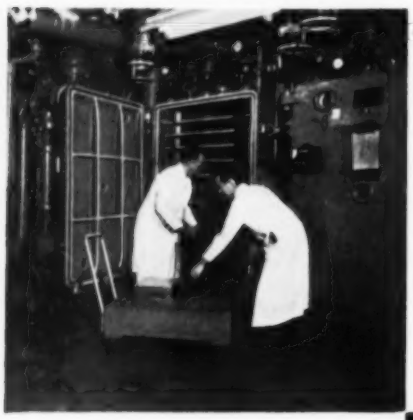

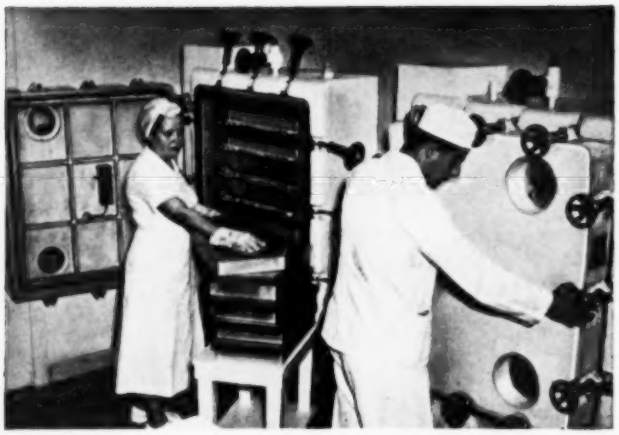

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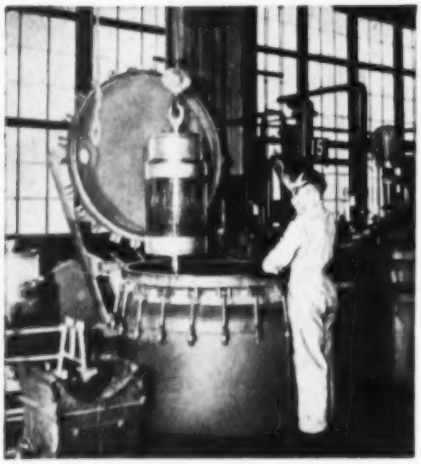

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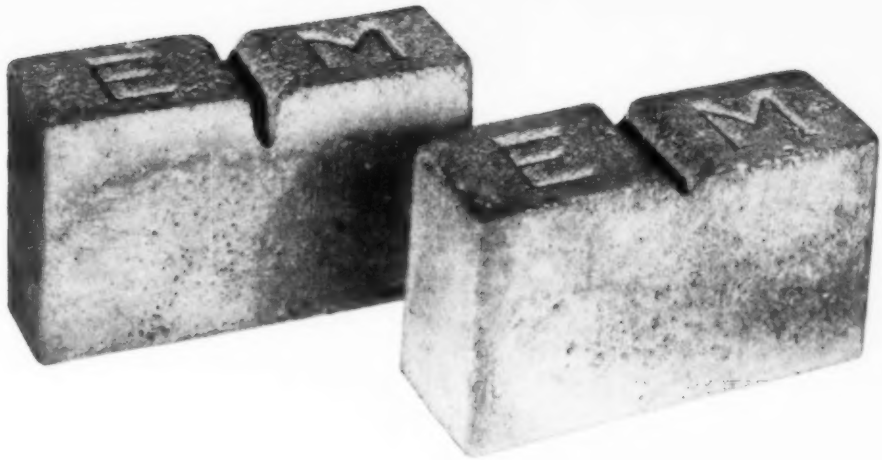

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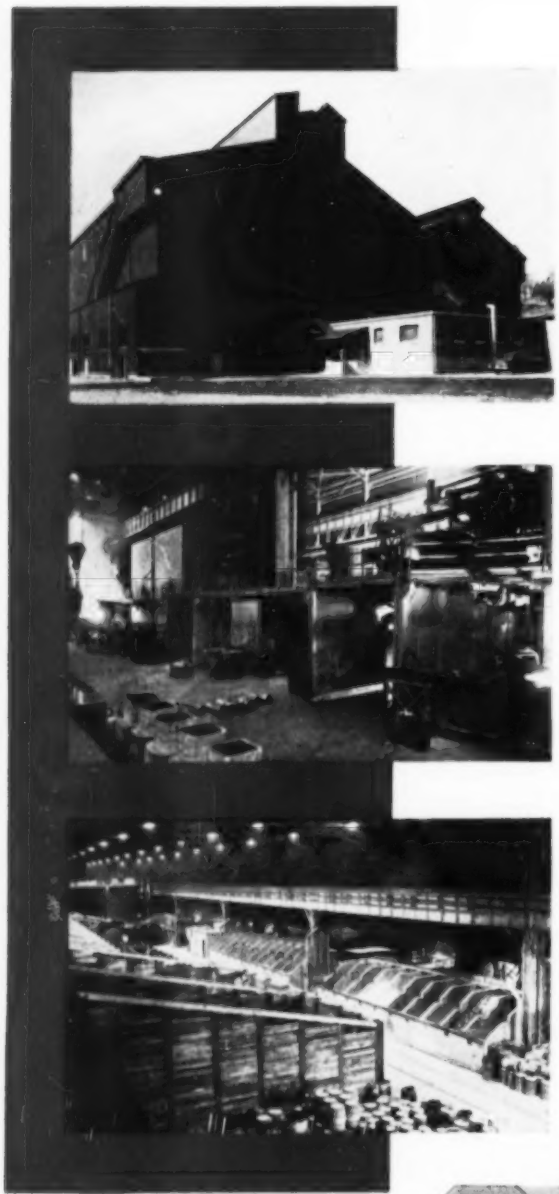

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4—FORK TRUCKS: High tiering model of Standard Skylift CF Line of electric fork trucks has been introduced by *Automatic Transportation Co.*

5—ALLOY: Development of K155, a new magnesium-type aluminum sheet alloy for general metalworking requirements has been announced by *Kaiser Aluminum & Sales, Inc.* This new alloy has the same general mechanical properties as the manganese type alloy 3S. It has a nominal magnesium content of 0.9 pct.

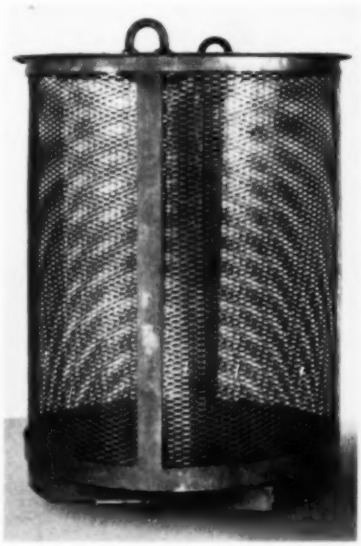
6—FOUNDRY SHAKEOUT: This line of equipment has been expanded by *Link-Belt Co.* A medium duty foundry shakeout in four sizes with capacities up to 5000 lb has been introduced.

7—MG HAND TRUCK: *Magnesium Co. of America* has announced a new magnesium hand truck weighing 18 lb., but its capacity tops 500 lb. All bolted construction enables easy replacement of parts.

8—CARBIDE TOOL SHARPENING: Based on use of low cost abrasive paper belts and a new type belt machine, this method will supplement or replace the diamond wheel method. Rough grinding is done on a standard grit 60 silicon carbide wheel. Finishing the sides and top of the carbide tip on the belt machine uses a Tri-M-Ite Resinite abrasive belt ranging from grit 60 to 150. *Minnesota Mining & Mfg. Co.*

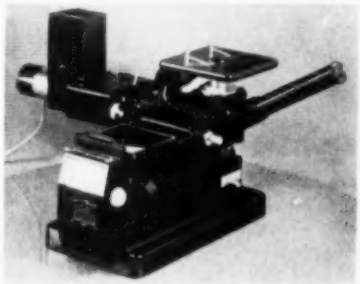
9—NORELCO STABILIZER: A tube current stabilizer has been announced by *North American Philips Co., Inc.* It is designed to hold tube current constant at any given setting when used in conjunction with the company's water-cooled X-ray diffraction equipment.

10—DEGREASING BASKET: Expanded metal provides maximum open area and penetration of liquid or air in basket made by *Stanwood Corp.* It is made by slitting and stretching solid steel sheet of various gages into 1-piece panels that



can be easily formed and welded to steel framework.

11—MICROSCOPE - METALLOGRAPH: A compact inverted design



provides handling ease and confines work area to 13x8x8 in. Group observation of the specimen is also made possible by projecting the light beam through the camera housing onto a screen. *Opplem Co., Inc.*

12—SPECTACLES: All plastic spectacle with a ball-chain hook design that fits comfortably behind the worker's ear has been announced by *Watchemoket Optical Co., Inc.* The plastic temples telescope in or out to adjust to any length.

13—PICK-UP TWEEZER: By depressing the top plunger of this instrument, three hooked, spring steel fingers extend from the tip and flare out. Releasing the plunger causes them to withdraw towards the tip and close. All stainless steel, the fingers extend to approximately 1¼ in. between tips. *Win Sales Co.*

14—X-RAY FILM HANGER: An X-ray film hanger and semi-automatic loader board that punches the film and guides the film hanger to instantly pick up the film has been announced. The hanger is of stainless steel to withstand corrosive effects of various solutions used in processing exposed X-ray film. *Hard & Co., Inc.*

15—MECHANOPRINT: A simple touch of the push bar causes the weight to be printed in this mechanical weight recorder. It is furnished with a variety of adaptations. *Howe Scale Co.*

16—LUBRICANT TUBES: A flat top gun lubricant tube and a long spouted bulk lubricant tube are offered by *Rockwell Mfg. Co.* for lubrication of Nordstrom valves.

17—COATING APPLICATOR: A special automatic spreader for applying protective wax coatings to cylinder gaskets has been designed by *Union Tool Corp.* Both sides are coated simultaneously and the coating rolls are felt covered; the doctor roll is neoprene covered. Maximum recommended coating speed is 20 lfpm.

18—PORTABLE WEIGHING UNITS: Self contained, portable hydraulic weighing units, accurate to 0.1 pct of scale, are now stocked in sizes up to 50 tons, according to *A. H. Emery Co.* Units are available in ranges from 0-500 lb to 0-100,000 lb.

19—WASTE PICKLE LIQUOR: Data on a new waste pickle liquor recovery process may be obtained from *Blaw-Knox Co.* The process recovers the entire sulphate equivalent of the waste pickle liquor as a reusable sulphuric acid without installation of expansive contact or chamber sulphuric acid plant.

Free Literature

20—AB METAL ANALYST: A comprehensive 200-page catalog of metallurgical apparatus is available from *Buehler Ltd.* The latest listing of cutters, grinders, mounting presses, microscopes, etc. is contained. A list of 250 recommended books for the metallurgical library is also included.

21—ANODES: The complete line of *Hanson-Van Winkle-Munning Co.* line of anodes, anode accessories, plating processes, and plating chemicals is described in bulletin AC-107.

22—CAPACITROLS: Wheelco capacitrol direct reading temperature controller is described in bulletin F-5783. Additional information on various models is also contained. *Barber-Colman Co.*

23—CASTINGS: Booklet devoted to the use of *Meehanite Metal Corp.* castings for component parts by the major machine tool manufacturers is available. Illustrations show the finished machine tool and indicate the specific Meehanite castings used in manufacture.

24—INDUSTRIAL CONTROLS: Catalog 8305 describes and illustrates nonindicating electric, electronic and pneumatic controllers for temperature, pressure, humidity. *Minneapolis-Honeywell Regulator Co.*

25—STAINLESS STEEL: A revised bulletin has been published showing complete line of stainless steel plates, forgings, sheets (No. 1 finish), tank heads, and flanges. *G. O. Carlson, Inc.*

26—URANIUM: The story of the Colorado Plateau's uranium industry is told in booklet published by *U. S. Vanadium Co.*

27—BELT CONVEYOR: Applications and features of the Rapistan Stevedore, Jr., portable belt conveyor have been printed by the *Rapids-Standard Co., Inc.* Specifications and features are given in chart and table form.

28—FLAME BURNER: Full size illustrations of the burners and the flame length produced by them are contained in bulletin issued by *Selas Corp. of America.*

29—MOUNT PRESS: Specimen mount press is described in bulletin issued by *Buehler Ltd.* Use of preheated premolds, rapid closing and universal application for thermosetting or thermoplastic materials in three sizes are features of the AB speed press.

30—METAL HOSE DATA: Information on application, temperature ranges of various types of hose, etc. is included in data book. Types of hose are illustrated and described. *Universal Metal Hose Co.*

31—RODINE: Pickling acid inhibitor is described in pamphlet released by *American Chemical Paint Co.*

32—ALTITUDE CHAMBERS: Test chambers for simulating various altitudes, temperatures and humidities are covered in bulletin announced by *Tenney Engineering, Inc.*

33—HEAT TREATING: Booklet issued by *Ipsen Industries, Inc.* explains Ipsen's 100 pct forced convection heat treating units. Cross-sections of the units, chart showing operational processes available, and complete specifications are included.

34—SAND PUMPS: Bulletin P9-B8 gives reasons why pressure molded rubber parts in *Denver Equipment Co.'s* SRL rubber lined sand pumps maintain high efficiency for prolonged periods. All parts are listed and also shown by sectional views. Clearance and foundation dimensions, specific gravity of pulps and other information are included.

35—ROTARY STRAIGHTENERS: Production experience records in straightening pipe and tubing at different plants are compiled in bulletin No. 52 published by *Mackintosh-Hemphill Co.* Data is presented in case study form.

36—CASTING IMPREGNATION: Development and application of modern impregnation of porous castings is described in bulletin issued by *American Metaseal Mfg. Corp.* Photographs show equipment used in bath immersion for rapid treatment of large quantities of parts, as well as applications in various metals.

Journal of Metals
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June

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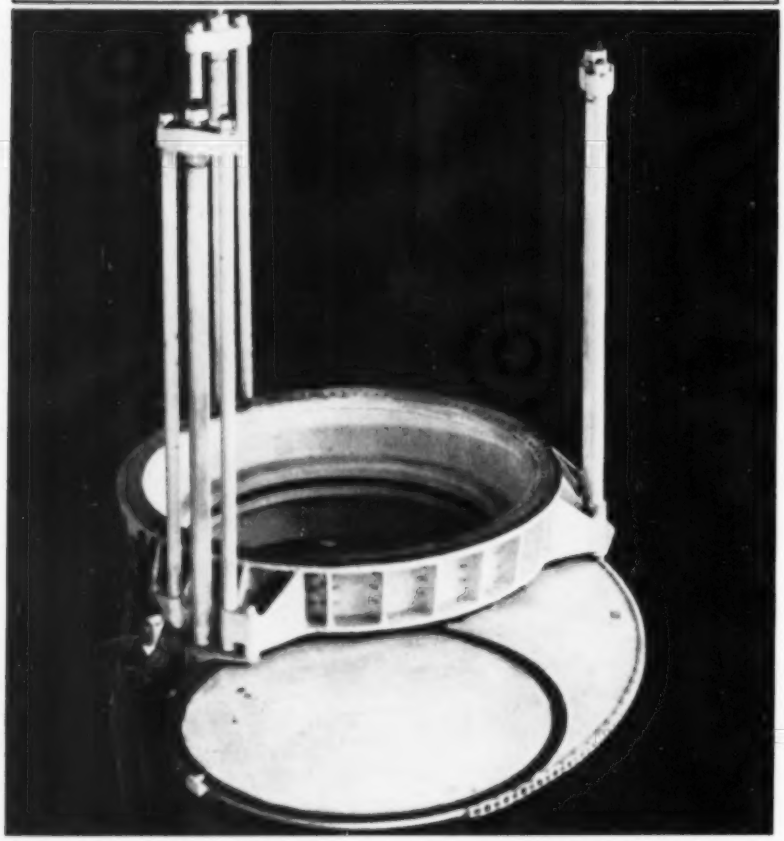
HOW A FORCE OF NATURE IMPROVES STEEL MILL SAFETY



Designed to protect men and equipment, this heavy duty Bailey Valve was produced for one of the nation's major steel makers. Although its diameter is 120" and its weight is close to 42,000 lbs., it is precisely machined to assure a tight, positive gas seal.

AN UNFAILING force of nature—the linear expansion and contraction of steel—is being used to increase steel mill safety. This powerful force, applied to Bailey Thermal Expansion Goggle Valves, provides a safe, dependable means of positive shutting off large gas mains in emergencies or for repairs.

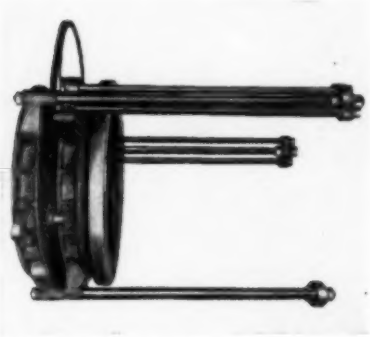
The Function of Goggle Valves

Ranging in diameter from 36" to 120", this type of valve long has been industry's standard method for controlling gas in the large mains for blast furnaces, gas washers and boilers. They take their name from one of their component parts—a large, moveable plate shaped like a pair of aviation goggles. This plate has one "goggle" open, the other of solid steel. When a gas main is in operation, the open goggle allows gas to flow through it freely; when the gas is to be shut off, the plate is moved until the closed goggle blocks the main, forming a tight, leak-proof seal.

BAILEY THERMAL EXPANSION GOGGLE VALVES

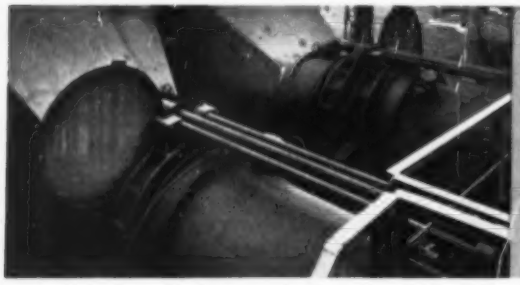
Safety and efficiency in closing the larger sized gas mains are provided by Bailey Thermal Expansion Goggle Valves. In them, the powerful force of linear expansion and contraction of three steel tubes is used to free or clamp the goggle plate—providing an absolutely gas-tight seal.

In operation, steam is passed into the tubes, which are spaced evenly around and perpendicular to the rigid steel flanges of the valve. The resulting expansion frees the heavy goggle plate so it may be swung to the open or closed position. When the steam is shut off, contraction of the tubes takes place, closing the flanges tightly against the goggle plate. Since both sides of the plate are machined to conform to the machined edges of the valve flange, Bailey Valves are leak-proof in both open and closed positions.



Bailey Thermal Expansion Goggle Valves are produced in diameters from 36" to 120".

Sound design and precision manufacture are combined in these valves to assure the ultimate in safety and reliability. They have been thoroughly proved on the gas mains of blast furnaces, gas washers and boiler plants. Bailey Thermal Expansion Goggle Valves are completely dependable in hot or cold, dirty or clean gas mains.



These valves are in service on an Elex Precipitator. In this view the goggle plates are in the open position.

WILLIAM M. Bailey COMPANY

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Books for Engineers

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Oxidation of Metals and Alloys, by O. Kubaschewski and B. E. Hopkins. *Academic Press, Inc.* $6.00, 239 pp., 1953.—The book is designed to bridge the gap between theoretical study and practical application. It provides an appraisal of the state of research in the field and gives an account of the existing ideas on the subject. Included is the examination of oxidation products, methods of measurement, protection of surfaces, and much fundamental data. More than 500 citations are presented in the list of references.

Manual for the Design of Ferrous and Non-Ferrous Pressure Vessels and Tanks, Fourth Edition, by Karl Siemon. *Edward Brothers, Inc.* $3.85, 284 pp., 1952.—Properties and fabricating characteristics of the principal metals used, both ferrous and nonferrous, are discussed in Part I. A detailed treatment of the design of pressure vessels and tanks is presented in Part II. Revisions and corrections bring the manual into line with the established codes for power boilers and unfired pressure vessels and with current practice. Arrangement is similar to earlier editions, with a technical data section at the back. A brief supplement on hoop design is appended.

Modern Mass Spectrometry, by G. P. Barnard. *The Institute of Physics.* $7.15, 324 pp., 1953.—The author's aim in writing this book was to collect and critically discuss the body of knowledge and technique concerning the mass spectrometer and its uses in most branches of applied and pure science. The monograph opens with the general theory of the instrument. Chapters on ion sources, vacuum techniques and gas-flow problems applying to mass spectrometry on the collection and measurement of ion beams and the associated electronic devices. After discussion of certain existing research and industrial instruments, five chapters are devoted to applications in physics, chemistry and engineering, to hydrocarbon analysis, to studies of molecular structure and chemical kinetics, to applications of isotopic tracer techniques to biochemistry and to isotopic studies in geology and nuclear chemistry.

World Production of Raw Materials. *The Royal Institute of International Affairs.* $1.50, 104 pp., 1953.—This book was published with the advice and help of Ronald Brech of the *London Economist.* The first chapter of the book begins with an assertion that world manufacturing is outstripping world supply of raw materials. After a discussion of the Malthusian theory, the book attempts to answer such questions as what is a raw material, geographical distribution, trends in production, experiments in international cooperation, and current developments in output. Iron and steel, steel alloying elements, nonferrous metals, and non-metallic minerals are discussed. Tables of world production are presented for metals and other raw materials.

Electrodynamics, by Arnold Sommerfield and translated by Edward G. Ramberg. *Academic Press, Inc.* $6.80, 371 pp., 1952.—General fundamentals and basic principles of Maxwell's electrodynamics are discussed in Part I. The several classes of phenomena, in static, stationary, quasistationary, and rapidly variable fields are derived from Maxwell's equations in Part II. Treatment of the theory of relativity and electron theory in Part III is limited to the special theory of relativity and the theory of the individual electron. Part IV develops the electrodynamics of moving media. Waveguides and other special topics are considered in their proper place.

Equipment for the Thermal Treatment of Non-Ferrous Metals and Alloys. *Institute of Metals, London.* $2.50, 104 pp., 1953.—Seven papers deal with the following topics: Electric furnaces; gas equipment for heat treatment; batch and continuous annealing of copper and copper alloys; bright annealing of nickel and its alloys; batch heat treatment of light alloys; flash annealing of light alloys; and continuous heat treatment of aluminum alloys of the Duralumin type.

Heating, Ventilating, and Air Conditioning Guide. *American Society of Heating and Ventilating Engineers.* $7.50, 1560 pp., 1953.—This is the 31st edition of this standard work. New chapters in the book contain information on snow melting, water vapor and condensation in building construction. Chapters on electric heating and industrial exhaust systems have been completely rewritten. New information has been added on industrial oil and gas burners, short chimneys, industrial degree-days, warm air system design and unit heaters.

Engineering Valuation and Depreciation, by Anson Marston, Robley Winfrey, and Jean C. Hempstead. *McGraw-Hill Book Co.,* $8.00, 508 pp., 1953.—The text deals with the concepts and procedures in appraisal of industrial, commercial, utility, and natural resource property. Application is illustrated by specific examples. There are complete and detailed discussions on depreciation, service lives, limited-life enterprises, and a comparison of depreciation methods when applied to property groups as distinguished from single units. Court decisions which effect valuation practice are presented.

Synchros, Self-Synchronous Devices and Electrical Servo-Mechanisms, by Leonard R. Crow. *Scientific Book Publishing Co.,* $4.20, 222 pp., 1953. —The book's purpose is a contribution to a broad understanding of the fundamental principles of the functional operating theory as well as effective application of synchros and allied self-synchronous electrical mechanisms.

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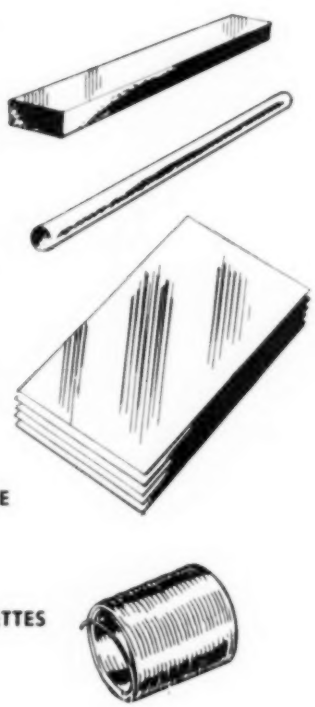

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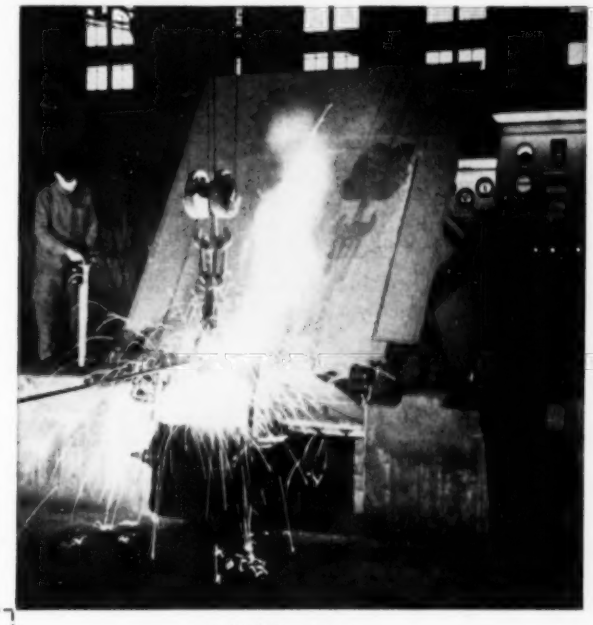
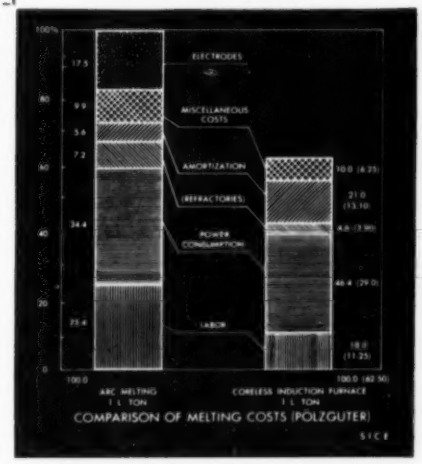


▲ High frequency installation in operation

◀ 10 ton high frequency furnace casing

▼ Comparison of Melting Costs



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Industrial Notes

• The Watson-Stillman Co., div. of H. K. Porter Co., Inc., Roselle, N. J. announced completion of a 1250-ton long stroke aluminum extrusion press capable of handling billets up to 24 in. long. Loading billet and dummy block into the container on a single forward stroke of the main ram is permitted by the long stroke design of the main cylinder. Die changing is possible in seconds because of the U-shaped opening of the die slide for mounting the die ring and bolster. Operation sequence is semi-automatic. Interlocks protect all mechanisms and limit switch adjustment for setting thickness of butt.

• *First seamless drawn aluminum tubing produced west of the Rockies by Revere Copper & Brass Co., came out of the firm's Pacific Coast div., at Los Angeles. Seamless aluminum tubing is the first of a series of products to be produced on the coast by Revere. Output of other extruded aluminum shapes is expected in the near future. Facilities at the Pacific Coast div. were expanded last year to make the additional production possible.*

• **Extension work on the Royal Ave. building of the metals research laboratories of Union Carbide & Carbon Corp., at Niagara Falls, N. Y. will approximately double existing facilities. The work on the L-shaped wing represents Electro Metallurgical Corp.'s part in a program expanding study in chemistry, metallurgy, and welding. The wing is expected to be ready for use in late fall.**

• The new Atomic Energy Commission laboratory operated under contract by American Cyanamid Co., at Winchester, Mass., is in full operation. Primary objective at the laboratory is development and improvement of processes for recovery of uranium from its ores.

• Pittsburgh Steel Co. announced the start of operations of its new casing finishing department at Allenport, Pa. The $2 million installation can turn out enough steel casing to line two 12,000-ft deep oil wells in 8 hr. Seamless steel casing is manufactured on a high speed automatic No. 3 mill at the rate of 40 in. of pierced billet per sec. The four threading machines, coupling screw-on machine, and the hydrostatic test bench are automatic. Monthly production is expected to reach 10,000 to 12,000 tons when the department swings into high gear.

• *American Pulverizing Co. has built a crusher capable of handling a 50-ton carload of scrap. The machine reportedly can crush scrap three to five times faster than any prototype. The machine stands 13 ft high and covers a floor area of 10 sq ft. The company claims that the crusher is the largest of its type ever constructed.*

• **Loftus Engineering Co. engineers say they have established a new speed record for induction heating of a 30-in. diam aluminum billet weighing 4300 lb. Loftus heated the aluminum cylinder to 760°F in 31 min. The new low-frequency induction heater has been on display to industry representatives.**

• Two Italian imports are attracting attention. One is a new

NEW BUEHLER CATALOG

200 pages — a comprehensive catalogue of Buehler equipment for the metallurgical laboratory. Includes sections on Cutters, Grinders, Specimen Mount Presses, Polishers, Metallographs, Microscopes, Cameras, Testing Machines, Spectrographs, Furnaces and other equipment for the metallurgical laboratory.

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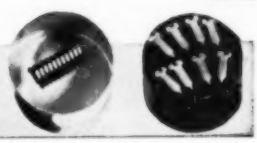

metallurgical microscope and metallograph made by Officine Galileo, requiring only one tenth of the space formerly required for this type of instrument. The second, by Galileo, is a CZ microscope magnifying from 4X to 3000X continuously on the ground glass of the camera. Macrophotography down to 5X is possible without disturbing the specimen.

• Work is progressing at the Mullins Mfg. Corp. plant at Warren, Ohio, on a $2.6 million addition for the manufacture of commercial products via the firm's Koldflo steel process. Presently, Mullins is devoting the process to production of military artillery shells. The new facility at Warren will include four long stroke, 3000-ton presses, and two 2000-ton presses. Completion of the plant is scheduled for November 1953.

• What is believed to be one of the first privately financed atomic manufacturing plants is under construction near Pittsburgh, Pa., for manufacture of parts for atomic power plants. The multimillion dollar facility is scheduled to house the newly-formed Atomic Equipment Dept. of the Westinghouse Atomic Power Div. The building will consist of one floor covering some 87,000 sq ft, with about 200 persons employed in the operations. Completion and occupancy is expected this year, according to William C. Miller, manager of the Atomic Equipment Dept. Initial investment will be more than $1 million.

• *Contracts totaling $1.6 million were signed for complete porcelain enameling departments for two plants under construction by Westinghouse Electric Corp. Ferro Corp., of Cleveland, was awarded the contracts for the $20 million structure at Columbus, Ohio, and the one at Vicksburg, Miss. Ferro will furnish and install two large U-type enameling furnaces, spray booths, and continuous dryers, plus cleaning and pickling equipment at Columbus. At Vicksburg, Ferro will supply and install a continuous pickling and cleaning machine, automatic spray equipment, continuous monorail conveyors and U-type continuous enameling furnace.*

• First investment casting plant established in the Pacific Northwest is operating. The plant was built by Precision Castparts Corp., at Portland, Ore. Present facilities occupy 8000 sq ft. Equipment includes wax injection machines, burn out furnaces, steel melting furnaces, tool and die equipment, grinding and finishing equipment. The plant has its own metallurgical laboratory.

• American Cladmetals Co. stockholders voted overwhelmingly for a proposed merger with Salem-Brosius. Name of the new firm will be Salem-Brosius, Inc., with management to be taken over by the existing Salem-Brosius personnel. Former activities of Cladmetals will be assigned to a division of Salem-Brosius. Design of industrial heating furnaces and steel mill equipment will be continued by Salem-Brosius. The new group intends to expand activities into the former cladmetals plant in Carnegie, Pa., as soon as is feasible without production schedule interference.

• An order for two self-contained hydraulic extrusion presses was placed with Hydropress, Inc., N. Y., by Reynolds Metals Co., of Richmond, Va. The presses are of advanced design and will permit Reynolds to expand its extrusion operations.

Will X-Ray Diffraction Reveal the Hidden Secrets

of Cancer . . . Heart Diseases . . . Hardening of Arteries?

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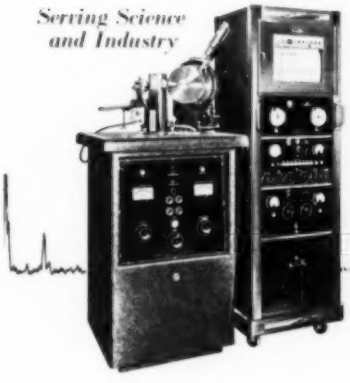

DOCTORS at New York's Mount Sinai Hospital are using NORELCO X-ray Diffraction equipment designed by Philips—world leader in X-ray development — to observe molecular behavior in the calcium salts of bone cancer, calcium salt deposits in artery walls, and the composition and formation of kidney stones. New observations have been made concerning heart structure and behavior. In X-ray Diffraction, there is indeed new hope.

Applied to industry, NORELCO X-ray Diffraction equipment has already revolutionized metallurgical and chemical methods — improved controls for production, processing and end-product analysis.

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You may find NORELCO X-ray Diffraction equipment just as valuable for your company or research organization. Write for free consultation. Also free booklet—"What is X-ray Diffraction?"

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. . . but one does more!

HERE you see two pieces of steel. They are the same size, the same shape, the same weight. Although they look exactly alike, one of these steels is far more valuable—in terms of what it can do for you.

It's the piece on the right—one of the U·S·S High Strength Steels—and it has greater strength than the ordinary carbon steel shown on the left. This means that with U·S·S High Strength Steel you can reduce the weight of a railroad car . . . a truck . . . a bus . . . or of many other steel products . . . *without reducing their strength.*

U·S·S High Strength Steel in a ¼" thickness can frequently be substituted in a design which uses ⅜" ordinary carbon steel, without sacrificing strength in the equipment.

Or—you can work it this way. Simply use U·S·S High Strength Steel in the *same* thickness as ordinary carbon steel. Then, your equipment will be stronger and more rugged . . . but it will weigh no more!

Furthermore, one of these high strength steels—U·S·S COR-TEN—has high resistance to atmospheric corrosion—4 to 6 times that of plain steel. Think what this means in increased life!

Very fine, you say, but what will all this cost? Well, here's the real pay-off. Surprisingly enough the products improved with U·S·S High Strength Steels usually cost no more . . . because pound for pound the steel does more. Its slightly higher initial cost per pound is often offset by the fact that less steel is needed. And, in the long run, many products made from these better steels actually cost less because they last longer, and are cheaper to operate and maintain.

1933 USS HIGH STRENGTH STEELS UNITED STATES STEEL 1953
TWENTY YEARS OF PERFORMANCE

JUST 20 YEARS AGO the first heat of the best known of these high strength steels—U·S·S COR-TEN—was shipped to a customer. Since then over 2 million tons of these "steels that do more" have been produced. They have been used to make more than 170,000 freight cars lighter or stronger . . . to build buses lighter and more efficient . . . to save weight in trucks so they can haul more payload . . . to make mine equipment and earth-moving machinery stronger and tougher . . . to give the farmer strong and durable tractors and implements. L-P gas cylinders, water heaters, and a multitude of other products last longer, are easier to handle, cost less to make and ship because they are made with U·S·S High Strength Steels. If you'd like to add their money-saving advantages to your product, write us. United States Steel Corporation, Room 7813-R 525 William Penn Place, Pittsburgh 30, Pa.

UNITED STATES STEEL

Within the few short years that rare earths have been commercially available, mining and refining operations have been tremendously increased. The pick and shovel mining has been replaced by large scale earth moving equipment to keep pace with increasing demand.

Operating the world's largest rare earth deposits, the Molybdenum Corporation of America has recently conducted extensive pioneering research in evaluating the properties, applications and uses of Rare-Met T Compound.

For example, in stainless steel, excellent results have been demonstrated in hot workability and increased shipping yield. In nodular iron, small additions of rare earths have helped to produce consistently good ductility by counteracting tramp elements such as lead and titanium.

As recognized authorities in the application of Molybdenum, Tungsten, Boron, Rare Earths, and the alloys and chemical elements of these materials, MCA assures confidential and immediate response to inquiries.

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CORPORATION OF AMERICA

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Sales Representatives: Edgar L. Fink, Detroit; Brumley-Donaldson Co., Los Angeles, San Francisco
Subsidiary: Cleveland Tungsten, Inc., Cleveland
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MCA

ABOUT 75 pct of the 205,000 tons additional annual smelting capacity authorized by the Government since 1951 for Aluminum Co. of America has been added to the firm's output. The goal has been set at a total of 550,000 tons. Alcoa hopes to hit the target by spring 1954. To date, one facility has been expanded and two others are reaching the end of construction.

The additions were made at Point Comfort, Texas, where two new smelting units are in use, increasing aluminum production capacity by 35,000 tons annually. The new plant at Wenatchee, Wash., with four potlines in operation since last June, is rapidly approaching capacity of 85,000 tons annually. The four lines are operating but not at capacity. Another 85,000 ton capacity plant is going up at Rockdale, Texas and when completed will be the first one to use electric power generated by burning lignite. The plant, scheduled for summer completion, will also have four potlines.

Other Alcoa developments are moving along. Additions have been made to the company's fabricating equipment, and other installations. Full capacity is expected at the alumina plant at Bauxite, Ark., by mid-summer with an annual output of 400,000 tons. At Mobile, Ala., expansion is expected to give the plant there an increase of 200,000 tons of alumina per year. When capacity is reached in the near future production is expected to total some 875,000 tons of alumina annually. When Alcoa finishes its share of the present aluminum expansion program for the nation, the company will have spent more than $350 million. Primary aluminum production expansion for the nation as a whole is being geared to a hoped for 1.5 million ton per year output by 1954. Total U. S. production in 1939 was slightly more than 163,000 tons, one ninth of current capacity.

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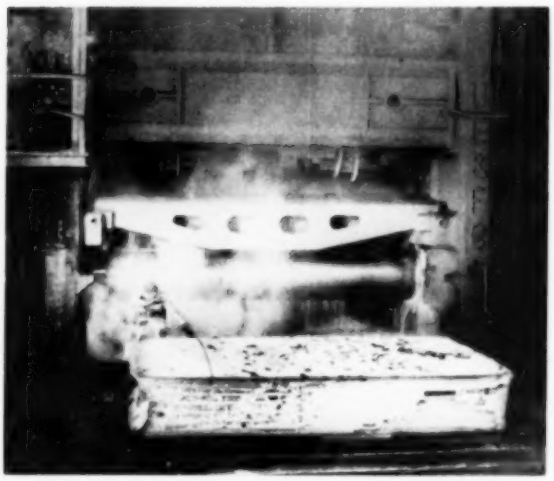
OVER the years many plans have been proposed, but American colleges and universities still face tremendous financial problems. Schools require money to train the men needed to continue American leadership in world industry. Many a good lad fails to get to college because the money just isn't there. It's tough to work one's way through school when dollars are needed for basic necessities of the family. Short of Federal subsidization, which many college heads reject, the only answer seems to lie in the direction of increased aid through wider distribution of scholarships. Industry cries for engineers —and the colleges turn out less than what is needed. While a good part of the reason lies with the personal choice of the student—many just can't afford to travel the road of science curricula.

Lately, business has been thinking of lending a hand to the nation's schools. But college deans and presidents have viewed the idea with about the same attitude held toward Government aid. One question arises: "What are the strings?"

Bethlehem Steel Co. answered the question recently. Instead of the direct scholarship or subsidization for a specific purpose approach, the steel company offered 45 private institutions $3000 for each graduate that is hired for Bethlehem's training course—and who stays four months.



Heavy plate is rolled on America's largest plate mill, Lukens 206-in. mill. Two electric motors developing 21,000 peak hp, power this 47-ft high mill, one of the first four high units in the U. S. It can roll ingots weighing 66 tons to 25-in. maximum thickness, 195-in. maximum width, or up to 840 in. long.

The money can be used as the schools see fit—"for scholarships, or any other purpose which best meets their needs." Eugene G. Grace, Bethlehem chairman, points out that "four years of college costs a college more than it receives from a student in tuition and other fees, and that the college graduate's education makes him a valuable asset in the conduct of Bethlehem's business."

Estimates of program cost place it at a possible $300,000 per year. While Bethlehem is primarily interested in engineering students, the firm is looking for men to fill positions in other departments. Sales, administration, operating departments, purchasing, and technical research personnel are in the field.

Starting this year with the current graduating class, the program is a long-range one. Mr. Grace recognizes that it may be a year or two before Bethlehem begins to see full benefits from the plan. Bethlehem's Loop Training Course takes on more than 100 men each year.

Bethlehem's approach may be the start of something new in the way of American education advancement. Certainly it will help meet bills and allow for hiring of additional faculty members.

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INTERNATIONAL Nickel Co., of Canada, Ltd., delivered 249 million lb of nickel in all forms during 1952. This represented some 75 pct of the nickel used by the free world, according to John F. Thompson, Inco board chairman. Underlying his summation of last year's activities were certain significant mat-

ters. Government restrictions on the end uses of nickel have definitely cut into outlets for the metal. "Some of our peacetime markets have been lost, but only temporarily," Mr. Thompson noted. Restrictions have also stopped effective development of new uses of nickel. Some markets may have even been "permanently diminished or even permanently lost," said Thompson. But new uses will be discovered, and certain uses now small, will be expanded when the defense demand slows.

However, preparedness has not been all black. It has enlarged the scope of experience with many alloys in many fields. During 1952 aircraft production in the U. S., the United Kingdom and Canada used great amounts of nickel-containing alloys. Greater consumption is foreseen in gas turbines and aircraft jet engines employed in civilian industry. In addition to the inauguration of regularly scheduled jet engine flights, experimental gas turbines in locomotives have proved successful enough to justify equipment orders.

Two important process developments at Copper Cliff were also noted:—The recovery of nickel and iron from nickeliferous pyrrhotite and oxygen flash smelting of copper concentrates. The oxygen flash smelting process has reached the point where by-product liquid sulphur is being delivered to Canadian consumers. First production unit using the pyrrhotite process is under design after successful pilot plant operations.

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U. S. ZINC smelters will produce an estimated 940,000 tons this year, according to a prediction made by Howard L. Young, American Zinc Sales Co. However, Mr. Young points out that predictions must assume "a sufficient supply of concentrates to U. S. smelters." American mining people predict that U. S. produced concentrates will be cut back if current price levels continue. However, stocks now in producers' hands, domestic production continuing at the current price level, and available foreign concentrates should be enough to allow domestic smelters to operate at near present levels.

Production of slab zinc in the U. S. during the last four months of 1952 and the first three months of 1953 was at an average of 80,000 tons per month. First quarter imports of foreign zinc during 1953 rose over that of 1952, with all grades available at low prices. Mr. Young estimates that a total of 180,000 tons of imports will come to the U. S. during the current year, making available to U. S. buyers some 1,120,000 tons. He estimates that U. S. will export only 12,000 tons, while Government stockpiles will get about 60,000 tons under sale contract and floor price contracts currently in operation. He deducts stockpile and exports to arrive at 1,048,000 tons of slab zinc available to U. S. consuming industry.

R. Lewis Stubbs, director of the Zinc Development Assn., Oxford, England, predicts that increased production in French African territories will raise mine production by some 40 to 50,000 tons over the 526,000 metric tons of 1952. Mr. Stubbs estimates consumption at 660,000 tons compared with 617,000 tons in 1952 and 713,000 tons in 1951. European consumption and production are not far from balanced. His figures, of course, are for Western Europe and do not include the Iron Curtain countries. Western Europe smelter production is expected to show some slight increase but "there may be small reductions in exporting countries such as Belgium, pending revival of demand." Mr. Stubbs points out that steps are being taken to revive the European demand.

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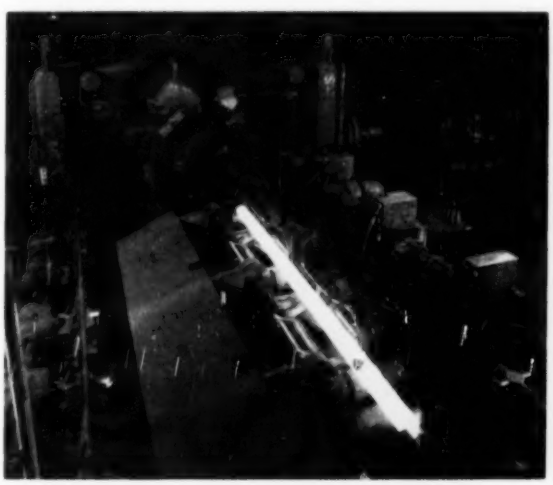
SUPPLY and demand in the steel industry may come into balance by the beginning of fall or a little later. Many steel executives in the Pittsburgh area hold this view and one even went as far as pinpointing the day—September 1. He refused use of his name, but according to newspaper reports announced his prediction for publication. The fall deadline is contingent on one vital factor however. Should the automobile industry continue to produce at the phenomenal rate of 7 million units per year the predictions are likely to be somewhat wrong. Another factor of course is the position taken by the United Steel workers.

There is yet another factor involved. If the balance is struck, what happens to steel production then? Some steel executives believe production will decline moderately and others feel it will continue on a high level. Demand is running strong now for two reasons. In addition to automotive demands, Government requirements for shell steel have jumped. Shortages still exist in certain steel categories despite predictions of softer markets to come.

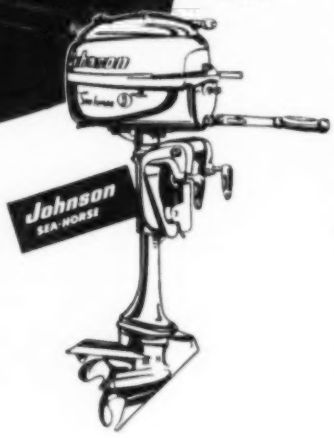


Steel and tube div. of the Timken Roller Bearing Co. installed a modern outlet table on its No. 2 piercing mill. The new table is equipped with roller guides which hold the mandrel bar and pierced tubing rigidly in position for piercing. It replaces a standard Mannesmann outlet table.

62 AJAX TAMA-WYATT Induction Furnaces—

help Johnson Motors produce millions of aluminum alloy die castings per year

Photo shows a part of the Aluminum Alloy Die Casting Shop at Johnson Motors.



Johnson Motors, Division of Out-Board & Marine Mfg. Co., Waukegan, Ill., has the largest aluminum die casting plant in the world using exclusively electric furnaces for melting and holding the metal to be processed in die casting machines for the production of outboard motors.

AJAX Induction Furnaces have proved most satisfactory for this concern because they have automatic temperature control, gentle movement of the metal (which prevents segregation), and amazingly low maintenance cost. Some furnaces have been operating for as long as 7 years without renewal of refractory lining.

"The best holding furnaces for aluminum die casting machines are considered to be electric induction furnaces. Where ingot is being added directly to the furnace for die casting, this is the only furnace on which there is little possibility of sludge formation at the bottom. The reason for that is obvious. The heat is where it belongs, down at the bottom of the furnace *in the metal*. Also, the agitation due to the internal electrical stirring, which has no effect on dross inclusions, gives the best conditions for holding furnaces (for either die casting or permanent molding), especially if it is desired to add pig directly to the furnace."

—From answer to "Quizmaster" question, provided by technical service staff at Federated Metals Div., American Smelting & Refining Co. in March 1953 issue of American Foundryman.

Write for Further Information to

AJAX ENGINEERING CORP., TRENTON 7, N. J.

AJAX TAMA-WYATT

INDUCTION MELTING FURNACE

AJAX ELECTRO METALLURGICAL CORP., and Associated Companies
AJAX ELECTROTHERMIC CORP., Ajax Northrup High Frequency Induction Furnaces
AJAX ELECTRIC CO., INC., The Ajax Wyatt Electric Salt Bath Furnace
AJAX ELECTRIC FURNACE CORP., Ajax Wyatt Induction Furnaces for Melting

Drift of Things

NOW it can be told! In October, JOURNAL OF METALS will publish its first Great Metals Enterprise issue, featuring the Colorado Fuel & Iron Corp. These issues will parallel the Famous Mining Enterprise issues of MINING ENGINEERING, which have become so well known throughout industry.

Much thought has gone into the beginning of the Great Metals Enterprise series, on our part as well as that of CF&I. We were extremely pleased when we received the go ahead from Al Franz, CF&I's president, who is certainly no stranger to the AIME Iron & Steel Div., especially the National Open Hearth Steel Conferences. So pleased in fact, that we cannot resist the temptation to reprint his letter here:

"Following a review of the editorial content of the JOURNAL OF METALS and a proposal for your October 1953 issue, we are pleased to authorize JOURNAL OF METALS, the official publication of the Metals Branch, The American Institute of Mining and Metallurgical Engineers, Inc., to cover a complete study of the Colorado Fuel and Iron Corporation and its subsidiary companies.

"We realize that CF&I's program of modernization, improvement and diversification has attracted much attention in the metals industry, and that a thoughtful record of our advance may prove of genuine interest to your many loyal readers.

"Judging from your past editorial accuracy and thoroughness, we deem it a pleasure to have our staff work closely with your editors to the end that the October issue of JOURNAL OF METALS will stand as a creditable report on one progressive segment of the steel industry. You may be assured of our complete cooperation."

To date we have been able to visit the plant at Pueblo, Colo., Wickwire Spencer Steel Div. plant at Buffalo, N. Y., and John A. Roebling's Sons at Trenton, N. J. Before going to Pueblo, we spent some time in Denver with G. A. Sabin, A. M. Riddle, Charley Golson, Howard Hochstatter, and Jack Smolenske. Jack Lacey, editor of CF&I's *Blast*, took us through the Pueblo plant. At Pueblo we were privileged to attend part of the weekly superintendents meeting, presided over by Rudy Smith, works manager, and Jay Martin, vice-president of operations. R. A. Jackson and H. T. Pinkney took us to visit the Allen coal mine. In Buffalo, we met Al Giblin, and toured the plant with Chet Janecki. At Roebling's we were guests of Al Neroni, and Bob Lamborn conducted the grand tour.

Readers of JOURNAL OF METALS will get the complete story of all the CF&I operations from coast to coast without having to leave their seats. Articles will be written by operating personnel at each of the plants. More details on this special issue will appear from time to time.

THIS appears to be the year of innovations for us. At the Blast Furnace, Coke Oven and Raw Materials Conference in April, the first annual JOURNAL OF METALS Award was presented to F. M. Stephens, Jr., Benny Langston, and A. C. Richardson, of Battelle Memorial Institute. Their paper, *Reduction-Oxidation Process for the Treatment of Taconites* appears in abstract in this issue. The complete paper will appear in the *Proceedings* of the Blast Furnace, Coke Oven and Raw Materials Committee.

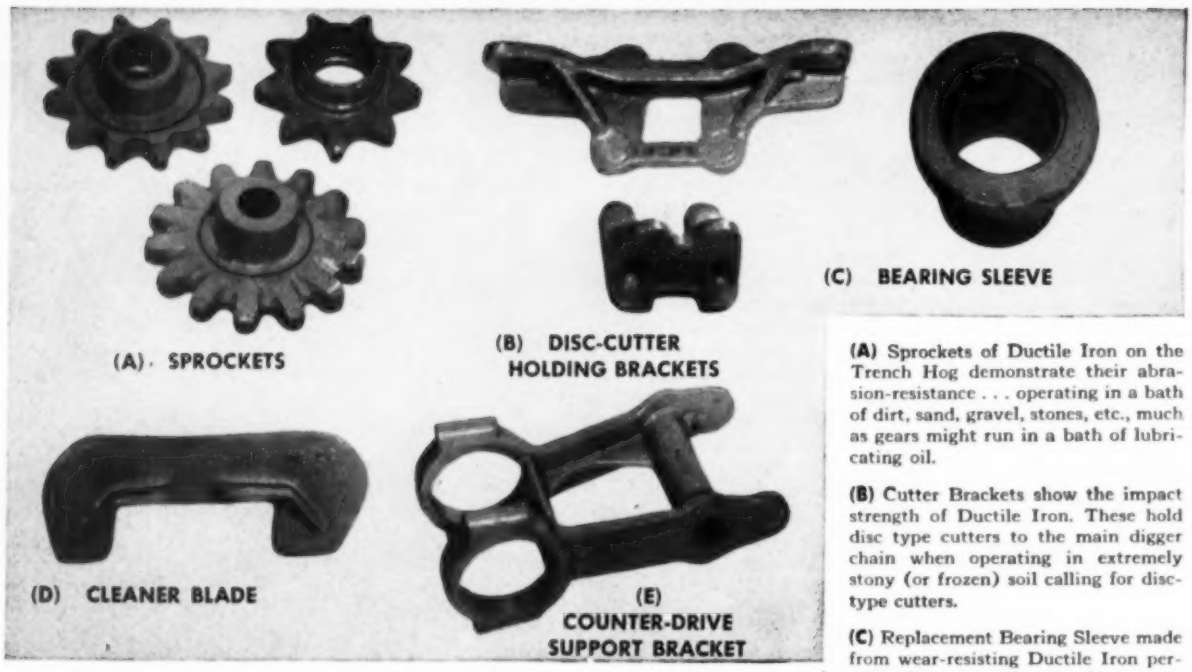
We heartily concur with the decision of the judges. Interest in the work has been great, and headquarters has been swamped with requests for copies of the paper. There can be no greater tribute for a job well done than the recognition of fellow engineers. Perhaps the word fellow should not be used—for the JOURNAL OF METALS Award rules state that there be no discrimination as to sex of authors of eligible papers.

RECENTLY, Ralph Goetzenberger, vice-president of Minneapolis-Honeywell Regulator Co. called to the attention of Engineers Joint Council an article that appeared in UNESCO *World News* on *Humanistic Problems in Technical Assistance*. The item, which was subsequently forwarded to AIME as a member of EJC, told of the complex nature of trying to introduce technical changes in some of the areas around the world. Even in a highly industrialized country, where changes from the old to the new are forever taking place, it takes a good while before people *accept* these changes. They tend to trust the old and familiar and resist the unfamiliar. Often it requires a highly organized advertising campaign before they agree to try a new improved product. This being so for highly developed countries, how much more deeply rooted this resistance to change must be in the world's nonindustrialized countries. There after all, life has altered little and slowly for hundreds of years. Drastic changes are difficult to get across, and a study of local cultures must be made to determine how to effect changes.

We were particularly interested in one of the ideas introduced, which will appear in a forthcoming publication of UNESCO called *Cultural Patterns and Technical Change*. It seems that in Thailand, a nutritional campaign was stalled because the people disliked cow's milk. The problem was solved when someone introduced canned milk. The cans, you see, gave the people no mental picture of a cow, and they were quite content to drink the white liquid that came out of tins!

A DISTINGUISHED visitor from London, whose name we are not permitted to mention, related this story at a recent luncheon. One morning, at a home in a somewhat remote and primitive area, the privy was found in the river that flowed beside the house. The father of the house demanded to know if his son had pushed the privy in the river during the night. "No sir," replied the son. The father then proceeded to relate the story of George Washington and the cherry tree, closing with, ". . and George Washington, having told the truth, was not punished." After the story, the father repeated his question, and the son replied, "Yes father, I pushed the privy in the river during the night." At this, the father began to thrash the son severely. "But father," he cried, "you said George Washington wasn't punished when he told the truth!" "Yes," replied the father, "but George Washington's father wasn't in the cherry tree when it was cut down either!"

Alvin S. Cohan



(A) Sprockets of Ductile Iron on the Trench Hog demonstrate their abrasion-resistance . . . operating in a bath of dirt, sand, gravel, stones, etc., much as gears might run in a bath of lubricating oil.

(B) Cutter Brackets show the impact strength of Ductile Iron. These hold disc type cutters to the main digger chain when operating in extremely stony (or frozen) soil calling for disc-type cutters.

(C) Replacement Bearing Sleeve made from wear-resisting Ductile Iron permits minimum wall section because its strength is much higher than that of gray iron, although it has the same machinability rating.

(D) Cleaner Blades of Ductile Iron mounted at regular intervals on the digger chain withstand battering and abrasion by stones and soil. These parts also prove the impact resistance of Ductile Iron.

(E) Counter-drive Support Brackets are subject to twisting action. Ductile Iron makes possible smaller, lighter brackets . . . with a higher safety factor against breakage.

Test DUCTILE IRON on Your Tough Jobs for a "SHOWDOWN" PROOF of its

- **Resistance to Wear**
- **Resistance to Impact**
- **High Strength**
- **Superior Machinability**

Only actual use can demonstrate the remarkable properties of Ductile Iron.

For Ductile Iron combines the *process advantages* of cast iron . . . such as good castability, ready machinability and moderate cost . . . with many of the *product advantages* of steel.

Several times stronger than ordinary cast iron, Ductile Iron also offers greatly increased shock resistance and ductility. As an example of some of Ductile Iron's many useful applications, look at the parts produced by STATE FOUNDRY AND MACHINE COMPANY, Cedar Grove, Wisconsin, for use on the Trench Hog digger manufactured by ARPS CORPORATION, New Holstein, Wisconsin.

Send us details of your prospective uses, so that we may offer a list of sources from some 100 authorized foundries now producing Ductile Iron under patent licenses. Request a list of available publications on Ductile Iron . . . mail the coupon now.

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THE INTERNATIONAL NICKEL COMPANY, INC. 67 WALL STREET NEW YORK 5, N. Y.

Sherritt Gordon is building a refinery at Fort Saskatchewan, Alberta that will employ a hydrometallurgical process for treatment of Lynn Lake nickel sulphide concentrate. The refinery is culmination of research involving Sherritt Gordon and Chemical Construction Corp. Page 775 of this issue of JOURNAL OF METALS contains comprehensive details.

A new process for the treatment of oxidized taconites combines a low temperature gaseous-reduction step and controlled reoxidation step with a direct heat transfer system giving a process requiring no external heat. Battelle Memorial Institute, with the sponsorship of several iron ore producing companies, conducted the project. Story of the process can be found on page 780 of this issue.

National Research Corp. announced a method for continuous reduction of zirconium by arc dissociation of halides. The process was developed under a research project sponsored by the Atomic Energy Commission. Corporation officials state that the method may be interesting for production of special grades of titanium and zirconium, but should not be considered a satisfactory approach for tonnage production.

Aluminum Co. of America is installing a 3-million lb stretcher at its Lafayette, Ind., works to straighten and relieve strain in large extruded aluminum parts. The stretcher is part of the U. S. Air Force heavy press program. The stretcher will be able to handle shapes up to 110 ft in length and up to 60 sq in. in cross-section of one of the strongest aircraft alloys, 75S.

A low shaft blast furnace designed for research on low grade fuels and ores for pig iron production is in operation at Liege. Belgium, France, Austria, Holland, Greece, Italy, and Luxembourg, as well as a U. S. institution supplied the funds for the experiment. British, Swedish, and Swiss specialists are at the disposal of the research committee. Schedules call for an output of 60 to 100 tons per day.

A new General Electric method permits manufacture of several thousand transistors from one ingot of germanium. GE can now produce 100 layers containing both germanium mixed with gallium and germanium containing small amounts of antimony. Schenectady Research Laboratory performed the research.

Silicon may soon be giving germanium competition in the transistor field if a new process for manufacturing pure silicon developed by the du Pont Co. lives up to expectations. Silicon may well broaden the scope of transistors because of its performance over a much wider temperature range than other available materials. Price is $430 per lb. Entire production is coming from a small pilot plant at the Newport, Del., plant of du Pont pigments dept.

Five of six Government owned magnesium plants have been ordered closed. The Velasco, Texas plant, operated by Dow Chemical Co., with a rated capacity of about 80 million lb per year, will stay open. Private capacity is rates at 56 million lb. Rated capacity of the six plants was 196 million lb annually.

NOW—

measure bath temperatures *this easier, better way*

New AUTOMATIC signalling features in the *ElectroniK* recorder bring greater simplicity and economy to the measurement of steel bath temperatures by the immersion thermocouple method. The instrument actuates remote color-coded lights near the furnace, to tell the operator when:

. . . thermocouple is properly connected and in operating condition.
. . . instrument is standardized and ready to record.
. . . thermocouple is preheated to correct temperatures.
. . . pen has recorded actual bath temperature.

The operator can make a complete measurement on signalled information alone . . . doesn't need to consult the *ElectroniK* recorder, which can be located remote from the furnace. Thermocouples last longer, because the operator leaves the element in the molten bath only long enough to get an accurate reading. This feature, in a typical installation, paid for the entire instrument cost in a single day.

The *ElectroniK* signalling recorder is equally applicable to measurements in the furnace or in the spoon. Our local engineering representative will be glad to discuss applications to your electric or open-hearth furnaces. Call him today . . . he is as near as your phone.

MINNEAPOLIS-HONEYWELL REGULATOR CO., *Industrial Division*, 4573 Wayne Ave., Philadelphia 44, Pa.

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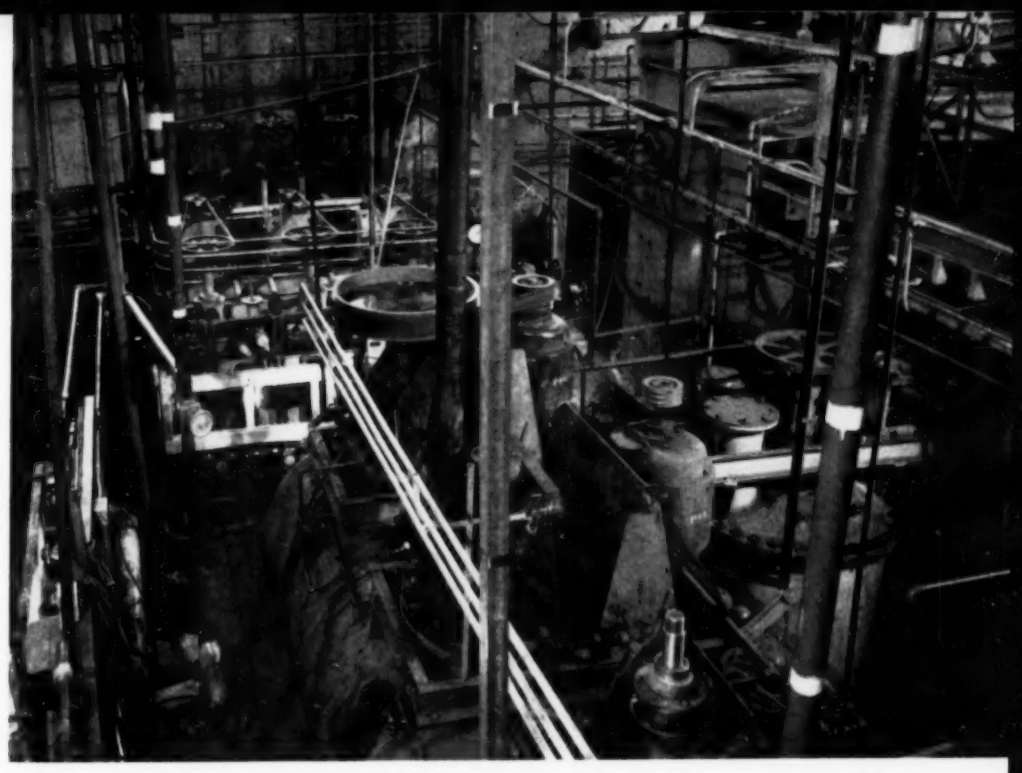


Final leach autoclaves can be seen in foreground of this view of the pilot plant. In the center is the adjustment leach autoclave, with the stripping autoclave at the rear. At the extreme right is the adjustment thickener. Wetted surfaces of autoclaves, agitators, pumps, valves, tanks, and pipelines are of stainless steel.

Hydrometallurgical Process Yields Pure Metal Powders From Sulphides

Here is the detailed story of the ammonia leach-hydrogen reduction process Sherritt Gordon will use for Lynn Lake nickel-cobalt sulphide concentrate. A $2.5 million research gamble, now backed by five years of intensive development in cooperation with the Chemical Construction Corp. resulted in a hydrometallurgical process offering savings of $2.5 million a year.

SHERRITT GORDON is building a refinery at Fort Saskatchewan, Alberta which will employ a hydrometallurgical process for treatment of Lynn Lake nickel sulphide concentrate at a saving of $2.5 million per year. The refinery, which will produce nickel and cobalt metal powders as well as ammonium sulphate, is the culmination of research involving Sherritt Gordon Mines Ltd. and the Chemical Construction Corp. in four pilot plants over a period of five years.

In 1947 Sherritt Gordon was developing a new mine at Lynn Lake, Manitoba. The company's operating property at Sherridon was rapidly nearing exhaustion. Preliminary work suggested that a hydrometallurgical process might overcome some of the drawbacks of conventional smelting of the nickel flotation concentrate to be produced at Lynn Lake, successor to Sherritt Gordon's Sherridon operation. Declining reserves at Sherridon, however, forced a five-year deadline on process development.

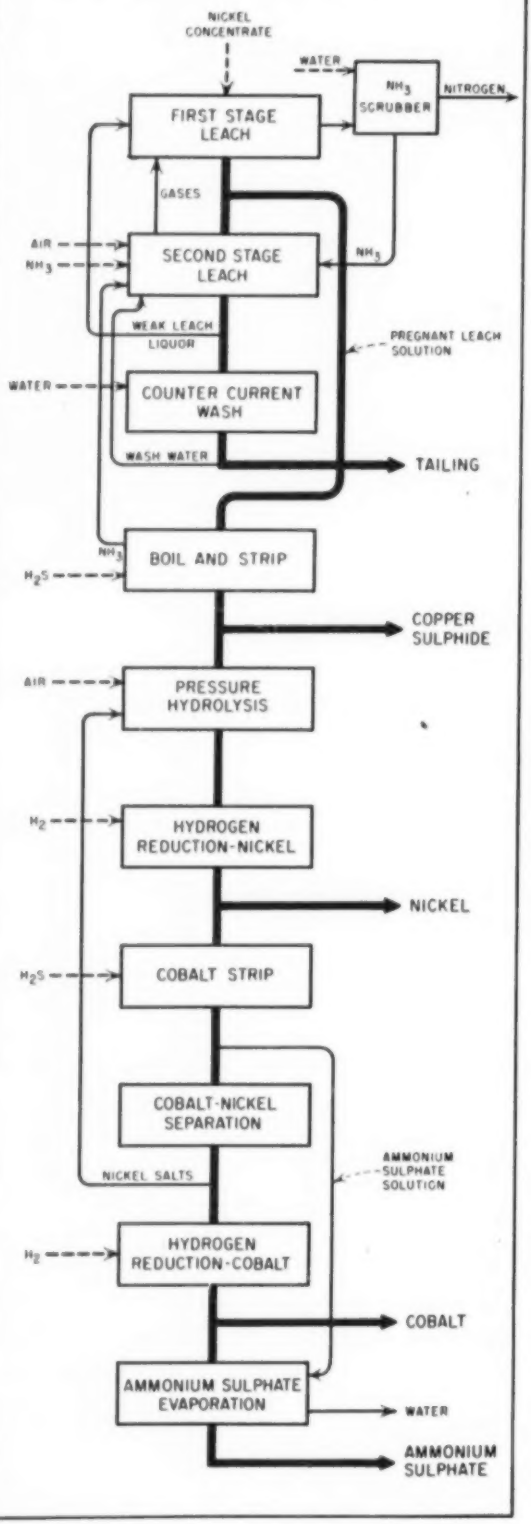
Five years and four pilot plant stages later Sherritt Gordon was able to finalize refinery design and began moving the 2000-ton concentrator from Sherridon to the new property at Lynn Lake, 150 miles farther north in Manitoba. Ore reserves developed at Lynn Lake amounted to 14 million tons carrying 1.223 pct nickel, 0.618 pct copper and some cobalt. Near Edmonton, Alberta, the nickel-cobalt refinery and chemical plant began to rise from the prairie.

Flotation testing of Lynn Lake ore readily produced a 30 pct copper concentrate and a nickel-cobalt concentrate with some copper content. Treatment of the copper concentrate by conventional smelting appeared economical. Nickel and cobalt recovery from the second concentrate presented more of a problem.

Conventional smelting and electrolytic refining for the nickel sulphide concentrate offered an estab-

Information for this article was largely supplied by Professor F. A. FORWARD, pioneer in the development of ammonia leaching techniques. Professor Forward is Head of the Dept. of Mining and Metallurgy at the University of British Columbia, where much of the research that laid the groundwork for the present process was carried out. He presented a paper, Leaching Nickel-Copper-Cobalt Sulphides with Ammonia Under Pressure at the 1953 Annual General Meeting of the Canadian Institute of Mining and Metallurgy.

FLOW SHEET OF AMMONIA PRESSURE LEACHING PROCESS FOR TREATING NICKEL-COPPER-COBALT CONCENTRATE



CHEMICAL REACTIONS

Unique in that nickel, cobalt and copper are extracted and recovered separately from a sulphide concentrate by hydrometallurgical operations only, the chemical foundations of the process lie in the equations given below:

Ammonia Leaching—Ammonia, oxygen and water react with the sulphide in an autoclave at 125 psi and 150° to 220°F to yield metal amines, hydrated iron oxide and ammonium thiosulphate;

$$2NiS + 8FeS + 14O_2 + 20NH_3 + 8H_2O \rightarrow 2Ni(NH_3)_6SO_4 + 4Fe_2O_3xH_2O + 4(NH_4)_2S_2O_3$$

and dissolved oxygen reacts further with the ammonium thiosulphate to produce ammonium sulphate and ammonium trithionate:

$$2(NH_4)_2S_2O_3 + 2O_2 \rightarrow (NH_4)_2S_3O_6 + (NH_4)_2SO_4$$

Further oxidation of the trithionate produces more ammonium sulphate and ammonium sulphamate:

$$(NH_4)_2S_3O_6 + 2O_2 + 4NH_3 + H_2O \rightarrow NH_4SO_3NH_2 + 2(NH_4)_2SO_4$$

At the end of the second leaching stage the hydrated ferric oxide, silica and insoluble compounds are filtered, washed and discarded. The two stage continuous counter current leach is carried out in a continuously operated compartmented autoclave. The first stage treats fresh concentrate with recycle liquor from the second stage and the partly leached solids go to the second stage where they are supplied fresh ammonia. Oxygen demand is lower in the second stage and increasing amounts of sulphate and sulphamate are formed.

Copper Removal—Boiling in a continuous still removes excess free ammonia and decomposes thio-

lished procedure, predictable operating results, and known design factors. Smelting would recover any gold and silver as well. On the other hand, costs would be high for labor, materials and power, especially in a remote area such as Lynn Lake. Precious metal content of the ore is less than 0.02 oz per ton and smelting would lose a major part of the cobalt.

Hydrometallurgical methods for recovering the nickel and cobalt promised to simplify materials handling, eliminate any dust problem, and instrumentation and automatic control in a hydrometallurgical plant would reduce required labor force.

Examination of possible treatment methods for Lynn Lake nickel-cobalt concentrate was undertaken in 1947. Within a year F. A. Forward and workers at the University of British Columbia found an ammonia leach that would do the job. Following early laboratory flotation testing a 50-ton per day pilot mill was set up at Lynn Lake that eventually provided over 350 tons of nickel concentrate for leaching studies. Work on this concentrate showed that nickel, copper, and cobalt sulphides could be dissolved without roasting if the proper temperature and pressure and concentration of oxygen and ammonia was maintained. The next step was development at the University of British Columbia and in Sherritt Gordon's laboratory at Sherridon of a means of separating the metals and the ammonium salts from the leach solution.

BEHIND THE FLOWSHEET

sulphate and trithionate as follows:

$$S_4O_6^{--} + Cu^{++} + 2H_2O \rightarrow 2SO_4^{--} + CuS + 4H^+$$
$$S_2O_3^{--} + Cu^{++} + H_2O \rightarrow SO_4^{--} + CuS + 2H^+$$
$$8Cu^{++} + 2S_2O_3^{--} + 4H_2O \rightarrow 8Cu^+ + S_4O_6^{--} + SO_4^{--} + 8H^+$$
$$2Cu^+ + S_4O_6^{--} + 2H_2O \rightarrow Cu_2S + 2SO_4 + 4H^+$$

Insufficient sulphide ion is produced to precipitate nickel, and the copper sulphide contains only about 1 pct nickel while the purified solution contains less than 0.005 g of copper per liter. While all the copper may be precipitated by the reactions above, it is convenient to remove the last traces of copper with small amounts of H_2S.

Hydrolysis—After removal of copper through the reactions above, remaining thionate and thiosulphate and sulphamate are removed to avoid high sulphur content in the nickel metal product. Oxidation under pressure converts the thionate to sulphate and hydrolyzes the sulphamate:

$$S_2O_3^{--} + 2O_2 + H_2O \rightarrow 2SO_4^{--} + 2H^+$$
$$S_4O_6^{--} + 2O_2 + 2H_2O \rightarrow 3SO_4^{--} + 4H^+$$
$$NH_2SO_3NH_2 + H_2O \rightarrow (NH_4)_2SO_4$$

Hydrogen Reduction—As shown by the reactions below, both cobalt and nickel compounds react the

$$Ni(NH_3)_2SO_4 + H_2 \rightarrow Ni^\circ + (NH_4)_2SO_4$$
$$Co(NH_3)_2SO_4 + H_2 \rightarrow Co^\circ + (NH_4)_2SO_4$$

same way when treated with hydrogen under pressure. Separate nickel precipitation, leaving cobalt in solution, is possible because the nickel reaction proceeds more readily. To minimize cobalt precipitation due to overlap of reaction conditions about 1 g of nickel is left per liter of solution.

Analysis of Flotation Concentrate Produced in the Pilot Mill

Nickel	10 to 14 pct
Copper	1 to 2 pct
Cobalt	0.3 to 0.4 pct
Iron	33 to 40 pct
Sulphur	28 to 34 pct
Insoluble	8 to 14 pct
Precious metals	less than 0.2 oz per ton

This nickel-cobalt concentrate appeared to give the best economic return, and was the material upon which process studies were based.

Recovery by Leaching, Based Upon Treatment of Flotation Concentrate

Nickel	90 to 95 pct
Copper	88 to 92 pct
Cobalt	50 to 75 pct
Sulphur	60 to 75 pct

Analysis of Metal Products, Pct

Nickel*		Copper Sulphide		Cobalt**	
Ni + Co	99.95+	Cu	70.0	Co	99.6
Co	0.10	S	22.5	Ni	0.15
Fe	0.01	Fe	1.5	Fe	0.20
S	0.01	Ni	0.9	S	0.02
Cu	0.01	Co	0.06	Cu	nil
		H_2O	balance		

*Meets specification for electrolytic nickel.
**Purity higher than normal market specifications.

Analysis of Ammonium Sulphate Product and Leach Residue, Pct

Ammonium Sulphate		Leach Residue	
N_2	21.0	Ni	0.60 to 1.40
S	25.1	Cu	0.20 to 0.25
Ca	0.07	Co	0.12 to 0.25
Fe	0.01	Fe	42 to 52
Mg	0.004	S	9 to 15
Ni	nil	Insoluble	12 to 16
Cu	nil		
Co	nil		

Two separate streams of research came together in December 1948, and out of their junction the present process was evolved. Chemical Construction Corp. was brought in to discuss engineering and design of a pilot refining plant. Independently, Chemico had been studying pressure leaching of sulphide ores with acid solutions. More important, they had discovered a means of nickel precipitation from ammoniacal solutions by using hydrogen under pressure.

Chemico's precipitation step vastly simplified metal production from the leach solution. When these two steps were brought together the final process began to take form; an ammonia leach as developed by Sherritt Gordon, followed by Chemico's pressure hydrogen precipitation procedure to recover nickel and cobalt metal from the solution.

Four Pilot Plants

Hydrometallurgical treatment of Lynn Lake nickel sulphide concentrate represents a long chain of work, a gradual scale-up of development stages. The third pilot plant provided data for design of the Fort Saskatchewan refinery, but research has not ceased and a fourth pilot plant now in operation embodies every stage of the full size plant now under construction. Complete instrumentation provides an opportunity for continuing study and a training ground for future operating personnel. In the words of C. A. Hames, manager of the metallurgical research div., ". . . the main objectives being to define the range of possible operating conditions and at the same time to train key personnel. . . It is hoped . . . the initial difficulties and adjustments of starting up the metallurgical plant will be minimized."

Cornerstone of any research program is adequate and representative testing material. In this case construction of a 50-ton per day pilot mill at Lynn Lake followed up early laboratory flotation testing.

Leaching tests at the University of British Columbia in 1947 and 1948 outlined a nickel recovery method that involved roasting, hydrogen reduction and leaching with ammonia and ammonium carbonate. During this work the basis of the present process was laid by discovery that under proper control of temperature, pressure, and oxygen concentration, ammonia leaching of the nickel, copper

and cobalt sulphides was possible without roasting and reduction treatment of the ore.

Next link in the chain of development was separation and recovery of the metals and ammonium salts from the leach solution. By December 1948 the first metal recovery method had been developed at the University of British Columbia and Sherritt Gordon's Sherridon laboratory. Nickel-ammonium sulphate was precipitated by boiling off ammonia and adding sulphuric acid. Precipitate was recovered by filtration. Further heating precipitated copper sulphide, and neutralization of the filtrate from the copper step precipitated cobalt sulphide. Ammonium sulphate was reclaimed from the end liquor by evaporation.

When the first pilot plant to employ the ammonia leach reached the planning stage discussion was started with the Chemical Construction Corp. on engineering and design problems and since that time a close association has been maintained between the two companies on development of the ammonia leach-hydrogen reduction process.

The first pilot plant, built in quarters of the Mines Branch at Ottawa operated during the next 14 months. Vital data provided at this stage were the possibility of substitution of air under pressure for the oxygen used originally to oxidize the concentrates in the autoclaving operation and discovery of a means of copper removal from the leach solution. Control of process to provide high enough concentration of trithionate and thiosulphate ions followed by boiling at atmospheric pressure, precipitated copper sulphide enabling precipitation of pure nickel metal in a subsequent operation.

Simplicity characterized the first pilot plant, aimed primarily at study of leaching under continuous operation. In 1950 the second pilot plant was built on semi-commercial scale incorporating nickel precipitation with hydrogen in high pressure autoclaves. Scale-up data developed during six months operation of this plant guided design of the third pilot plant completed in 1951. This third pilot plant was equipped for two stage counter current leaching of 3000 lb of concentrate per day, utilizing continuous equipment for filtering, washing and ammonia recovery.

Intensive operation of this plant resulted in some 60,000 readings and 14,000 laboratory analyses. These provided design data for the commercial plant now under construction that will treat 235 tons of nickel concentrate per day.

Sherritt Gordon hasn't ceased research—the fourth pilot plant is providing further process study and training future operating personnel.

Sequence of operations planned for the Fort Saskatchewan plant and used in the fourth pilot plant breaks down into two stages, leaching and metal recovery. The second stage successively yields copper sulphide, nickel metal powder, cobalt metal powder, and finally a major part of the ammonia and sulphur introduced to the operation are recovered as saleable ammonium sulphate.

Two stage leaching and counter current washing of the concentrate takes less than 24 hr in continuous operation carried out at about 125 psi and temperatures of 150° to 220°F. Sulphide minerals, ammonia, oxygen, and water reacting in the autoclave evolve more than sufficient heat to hold the leaching temperature. Amount of heat evolved, about 1500 Btu per lb of concentrate, is greater than that produced by roasting the same sulphide in air. Excess heat is carried off through cooling coils in the autoclaves. Wetted surfaces of autoclaves, agitators, pumps, valves, and tanks as well as the pipelines are of stainless steel. Corrosion and scaling have been of minor difficulty.

After filtering, the pregnant solution from leaching passes through a continuous still to remove any excess free ammonia. Boiling continues and the thiosulphate and trithionate decompose and copper sulphide is precipitated. Final traces of copper are stripped with H_2S. Purification of leach solution

Chronology of Sherritt Gordon Process Development

1946 Lynn Lake mine development under way—Sherridon mine exhaustion in sight.

1947 Laboratory work initiated to develop a hydrometallurgical process for nickel sulphide concentrate.

1948 Ammonia leach process found promising. 50-ton per day pilot mill produces nickel concentrate for process study.

1949 Chemical Construction Corp. joins research effort and supplies a nickel precipitation method. First pilot plant built.

1950 Second pilot plant built incorporates nickel precipitation equipment.

1951 Third pilot plant with 3000-lb per day capacity provides design data for commercial plant.

1952 Construction of commercial refinery begun at Fort Saskatchewan. 2000-ton Sherridon concentrator being moved to Lynn Lake.

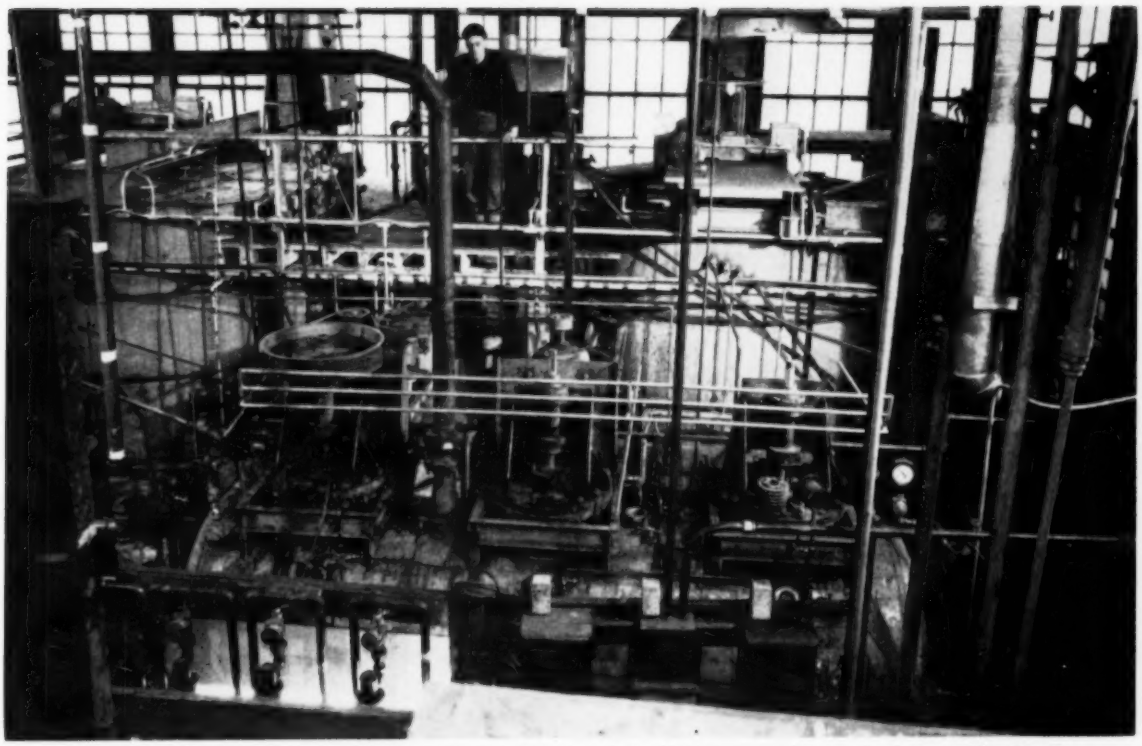
1953 Fourth pilot plant provides further research and trains key personnel. Production at Lynn Lake mine scheduled to start by end of year.

1954 Fort Saskatchewan refinery and chemical plant scheduled to start operation January 1.

Leaching and Hydrogen Reduction Finds Wide Use

Over the past year details were released on a hydrometallurgical process for recovering pure metal from sulphide concentrate. **Chemical Construction Corp.** played an instrumental role in the development of this process. First details were revealed by JOURNAL OF METALS in May 1952.

Five plants in three countries in various stages of planning, construction and operation testify to the rapid strides of the process. **Howe Sound Mining Co.** has a cobalt refinery coming into operation at Salt Lake City to treat concentrates from Calera, Idaho. In this $2.5 million plant an acid leach precedes cementation of copper, and cobalt precipitation by hydrogen under pressure. This process parallels that proposed for **National Lead Co.'s** $5 million plant being built at Fredericktown, Mo. to treat 50 tons per day of cobalt-nickel-copper concentrate. More recently, spokesmen of **Freeport Sulphur Co.** disclosed that Chemico's process for "the production of nickel as a metal rather than oxide, and also of cobalt" will be combined with Freeport's sulphuric acid leach to treat ore from the recently discovered Moa Bay nickel deposit in Cuba. **Sherritt Gordon's** refinery in Alberta will also use Chemico's metal precipitation technique, combined in this case with Sherritt's ammonia leach.



This is a broadside view of the final leach autoclave in the pilot plant. Thickeners can be seen in the rear. The Fort Saskatchewan plant for metal reduction by all wet chemical operations, based on pilot plant experience, will cost less than a combined smelting and electrolytic plant of equal capacity.

prior to hydrogen precipitation of nickel consists of heating with air under pressure to oxidize any remaining thionate to sulphate and hydrolyze sulphamate to ammonium sulphate. Until such time as arrangements are completed to leach the entire copper concentrate production of the mine, the copper sulphide produced in the refinery will be shipped to a smelter. It will be uneconomic to leach the small amount of copper in the nickel concentrate, about 5 tons per day, and precipitate copper metal powder with hydrogen under pressure.

Nickel is reduced first, although the cobalt salts react identically, because the cobalt reaction requires more severe conditions. There is some overlap of the range of reaction of nickel and cobalt and about 1 g of nickel per liter of solution is left unprecipitated so that a minimum of cobalt comes down with the nickel. End product of hydrogen precipitation is a nickel metal powder composed of spheroidal particles in the 50 to 80 micron size range.

Following nickel precipitation the solution is treated with H_2S to precipitate cobalt and the remaining nickel. Stripped solution produces crystalline ammonium sulphate by evaporation. Nickel-cobalt sulphide is releached with ammonia and oxygen and the cobalt separated. The remaining nickel, separated as a soluble salt, returns to the nickel precipitation circuit. The cobalt produced by hydrogen reduction under pressure is a 99.6 pct cobalt metal in powder finer than 50 microns.

Overall operation is simplified by elimination of any dust problem, and the fact that all materials are handled by pumps for solutions, and blowers for gases. The only reagents are ammonia, water, steam, hydrogen and hydrogen sulphide. Reagent feed is automatic and interlocked automatic controls result in maximum process control with minimum labor force. Not least important to the economics of the operation is that most of the sulphur is converted to readily saleable ammonium sulphate. A major product of the plant, of higher value than cobalt or copper, ammonium sulphate puts Sherritt Gordon into the chemical business on a large scale in Canada's booming Alberta province. In the future the plant will probably see wide diversification of chemical production with possible output of ammonia, ammonium sulphamate, copper sulphate and several other products in addition to present planned production of pure cobalt and nickel metal powders and of ammonium sulphate.

Research costs money, especially where a multitude of problems are to be solved in developing a new process for a new mine. And, these problems are further heightened when the work must be pushed as fast as possible to meet a deadline. Including estimated expenditure for 1953, Sherritt Gordon has $2,508,000 invested in research behind the chemical plant that is to treat 80,000 tons of concentrate per year.

In its new hydrometallurgical process for treating Lynn Lake nickel concentrate Sherritt Gordon has a process that is under control of the company. The plant for metal reduction by all wet chemical operation will cost less than a combined smelting and electrolytic plant of equal capacity. Most important, the ammonia leaching process should net a saving over conventional processes of some $2.5 million per year, a saving great enough to recover the total projected research and development investment in one year.

Journal of Metals Award Paper

Blast Furnace, Coke Oven and Raw Materials Committee, ISD

The Reduction-Oxidation Process For the Treatment of Taconites

New process for the treatment of oxidized taconites requires no external heat, has a recovery of iron units of 92 to 96 pct in magnetic form. This plus increased grindability of the processed ore indicates that the method will be economically attractive.

by F. M. Stephens, Jr., Benny Langston, and A. C. Richardson

THE problem of producing marketable iron ore concentrates from taconite, or iron range formation material, has received a great deal of attention within the past few years. Although most of base-metal production in this country is obtained from concentrates produced from ores which are relatively much lower in grade than taconite, the problem of concentrating low grade iron ores has not been easily solved because of several factors. Among these factors are the low unit value of iron ore, the tremendous tonnages used, and the variability of the formation material from which concentrates must be produced.

Four methods of concentration have been considered for treating the formation materials. They are gravity concentration, flotation, magnetic separation, and the conversion of hematite to magnetite followed by magnetic separation. To date, each of these four methods has had serious disadvantages which may be reviewed as follows:

Gravity concentration is a relatively inexpensive operation, but with finely disseminated materials such as taconite, the unit capacity of any gravity process is low, making it necessary to build large plants requiring a high initial investment. In addition, the recovery of iron units from most gravity concentration processes is low, a factor that makes mining costs high and is wasteful.

Flotation proved quite successful on some types of ore, but unfortunately the process is not adaptable to all types of taconites. Even more damaging is the fact that small amounts of some minerals, such as the Mesabi siderites, can ruin the selectivity of flotation processes on those ores which are normally amenable. A second serious disadvantage is that fine grinding, even past the true liberation point, is normally required to yield acceptable results.

Table I. Reduction Data[1] For Various Solid and Gaseous Materials

Material	Effective Temperature, °F	Amount Required[2]	Degree of Reduction, Pct
Hydrogen	750	2.0 x	96.2
Carbon Monoxide	660	2.0 x	93.0
Water Gas	750	2.0 x	93.2
Reformed Gas	750	2.0 x	92.1
Producer Gas	750	2.0 x	93.0
Methane	1110	16.0 x	97.0
Sawdust	1110	4.0 x	90.2
Peat	1110	4.0 x	93.4
Lignite	1110	4.0 x	89.5
Bituminous Coal	1110	4.0 x	91.9
Coke	1290	4.0 x	40.7
Siderite	1110	1.0 x	94.1

[1] Data are for 20-mesh ore treated for 60 min.
[2] Listed as multiple of the theoretical amount required to convert Fe_2O_3 to Fe_3O_4.

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Magnetic separation, an inexpensive high capacity operation, is already finding application on the formation materials which are primarily composed of magnetite. This process, however, cannot be used on hematitic ores or on ores where the iron content is equally distributed between hematite and magnetite.

Reduction followed by magnetic separation has always been an attractive method of treatment because of the high recoveries of iron that could be obtained almost without regard to the mineralogical composition of the starting ore. However, the high cost of furnishing the heat for a furnacing process has always led to the abandonment of the process as uneconomical.

Although a review of these four concentration methods shows that each has disadvantages, it also indicates that of the four, conversion of hematite to magnetite followed by magnetic separation is the most feasible if the economics can be made attractive. To improve the economics, two main lines of attack are open: Development of a low temperature process to cut the initial heat requirement, and development of a process in which heat may be recovered in usable form. The purpose here is to describe the reduction-oxidation process which accomplishes both of these objectives.

Process Development

The initial phase in the development of this process was a study of the reducing agents, to determine their effectiveness as a function of temperature and the amount required. The second phase of the development work was a study of heat-transfer systems. The results of this work were as follows:

Reducing Agents: The reducing agents considered for converting hematite to magnetite fall into two general classes: Gaseous reductants and solid reductants. The gaseous reductants tested were hydrogen, carbon monoxide, methane, water gas, reformed natural gas, and producer gas. The solid reductants tested were sawdust, peat, lignite coal, bituminous coal, coke, and siderite.

In evaluating the effectiveness of these reducing agents, three properties were considered: The lowest temperature at which rapid (30 to 60 min) reduction occurred; the degree of reduction obtained; and the amount of reductant required. A summary of the results obtained is given in Table I.

In general, the gaseous reducing agents which contain hydrogen or carbon monoxide, or mixtures of these two, are the most effective reducing agents for converting Fe_2O_3 to Fe_3O_4. They react at lower temperatures, give more complete reduction, and are effective in smaller quantities than are the other materials tested. For these reasons the logical choice for a commercial reducing agent appears to be a gaseous reductant containing hydrogen and/or carbon monoxide.

Heat-Transfer Systems: In previous reduction operations, about 50 pct of the entire cost of the process was chargeable directly to heating the ore to reaction temperature. It was realized at the beginning of this study that some method of recovering the sensible heat from the reduced ore must be employed if reduction to magnetite was to be made economically feasible.

Two heat-transfer systems were considered, indirect and direct. In the indirect system, the reduced ore would be quenched in water to produce steam which could be used for the generation of power or other useful work. In the direct system, the heat abstracted from the reduced ore would be used to preheat additional raw ore to the desired reaction temperature. The direct system appeared promising and was chosen for further development.

With the direct-heat-transfer system, it was necessary to find a medium which could be used to cool the reduced ore and could then be transferred to a point where it could be used to heat additional raw ore. An obvious answer was to use a gaseous medium such as carbon dioxide, steam, or nitrogen, all of which are inert and will not reoxidize hot reduced ore. However, it is expensive to produce any of these, and tests were undertaken to see if air might not be used as a heat-transfer agent.

These tests showed that if artificial magnetite is quenched in air at temperatures above 930°F, the magnetite is reoxidized to nonmagnetic hematite, but if the temperature is below 930°F, the magnetic properties are not destroyed. At the lower temperatures, the magnetite is also reoxidized, but gamma hematite, a highly magnetic material, is the oxidation product. Typical test results from some of the air-quenching studies are shown in Fig. 1. These same tests indicated that sufficient heat was released in this reoxidation step to be of material aid in the heat-transfer system.

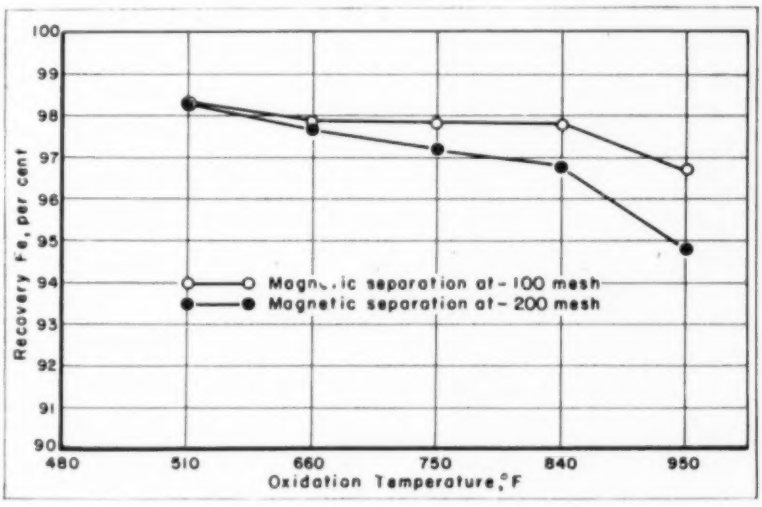

Fig. 1—This graph of the effect of quenching temperature on air cooling of −20 mesh reduced ore "A" is typical of the air quenching studies made. These tests indicated that sufficient heat was released in this reoxidation step to be of material aid in the heat-transfer system.

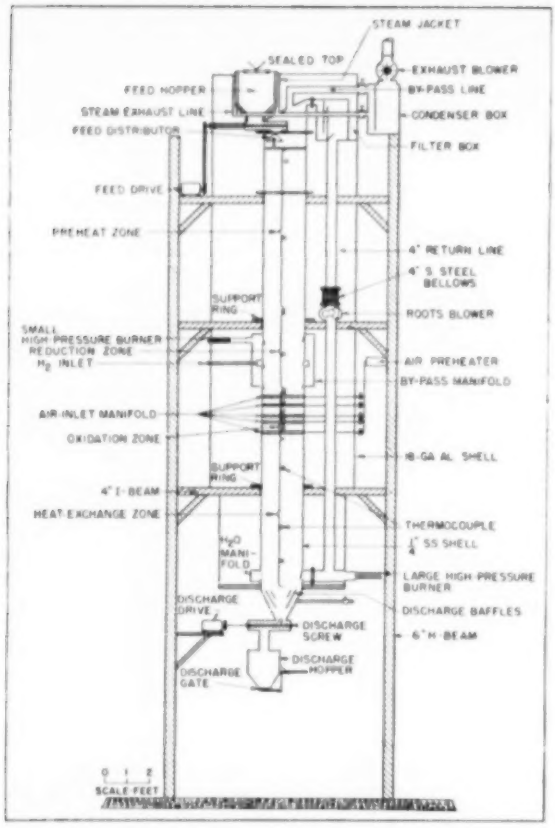

Fig. 2—This shaft-type furnace was constructed of metal rather than refractories because the temperature used for the reduction-oxidation process was only 930°F. This unit designed for operation with a feed rate of 200 lb of raw ore per hr, has been operated up to 600 lb per hr.

Gamma hematite has the chemical composition Fe_2O_3, which is the same as that of alpha hematite. However, gamma hematite has a cubic crystalline structure, whereas alpha hematite is rhombohedral. The difference in the magnetic susceptibility of the two minerals is apparently related to this difference in crystal structure.

When alpha hematite is reduced to artificial magnetite in the reduction-oxidation process, a change in crystal structure as well as a change in chemical composition takes place. Artificial magnetite has the chemical composition Fe_3O_4 and crystallizes in the cubic system. Upon reoxidation of the magnetite to gamma hematite, four oxygen atoms are added to the cube, and even though the chemical composition is again that of hematite, the crystal structure is basically that of magnetite and the high magnetic susceptibility remains. Because alpha hematite is the more stable form, gamma hematite may be classified as being in a metastable equilibrium.

Theory of the Reduction-Oxidation Process

Preliminary test work on the reduction of hematite iron ores to artificial magnetite at low temperatures by the use of gaseous reducing agents, and the possibility of using air as a heat-transfer gas for the recovery of the sensible heat in the ore, led to the development of the reduction-oxidation process.

This process has four basic steps. The first step is drying of the raw ore and preheating it to reaction temperature. The second step is the reduction of the hematite to artificial magnetite by means of one or both of the following reactions:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O - \text{heat}$$
$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 + \text{heat}$$

The third step of the process is the controlled reoxidation of the artificial magnetite to gamma hematite. This reaction is highly exothermic and is represented by the following equation:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3\ (\gamma) + \text{heat}$$

The final step in the process is the cooling of the gamma hematite to recover its sensible heat.

If certain limitations are observed, it becomes possible to operate the reduction-oxidation process in such a manner that it is cyclical with regard to heat requirements. The limitations are easily met when the process is used to treat oxidized taconites. The first of these limitations consists of having a sufficient quantity of iron present in the sample as hematite to form enough artificial magnetite to furnish the required heat in the oxidation step. This requirement means that the feed should contain at least 20 pct of iron present as hematite. The second limitation is that the artificial magnetite produced from the ore must be readily reoxidized at a temperature low enough to produce gamma hematite. The final limitation is that the ore must be readily reduced to artificial magnetite at a temperature below that required for reoxidation.

Most of the oxidized taconites examined contain 20 to 40 pct of iron as hematite which can be reduced at temperatures of 750° to 840°F and may be reoxidized to gamma hematite at temperatures up to 930°F.

A heat balance for a typical taconite being treated by the reduction-oxidation process is shown in Table II, which indicates a theoretical amount of excess heat equal to 23 pct of the heat requirement. This excess heat is available to balance radiation and other heat losses.

Table II. Typical Heat Balance For Taconite Treated in the Reduction-Oxidation Process

Basis: 2000 lb of ore containing 33 pct total iron, 22 pct iron as hematite, and 2 pct moisture

Heat Required	Btu
For evaporation of 2 pct moisture	40,000
To raise ore to 750°F	325,000
To raise H_2 to 750°F	10,000
For reaction $3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$	10,250
Total required	385,250

Heat Available	Btu
Sensible heat from ore at 750°F	325,000
From reaction $4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$ (γ)	148,000
Total available	473,400

Excess heat available per short ton: 473,400 − 385,250 = 88,150

Pilot Plant Construction

To test the feasibility of the reduction-oxidation process on a continuous basis, a small pilot plant furnace was constructed. This unit had a nominal capacity of 200 lb of ore per hr.

The main requirements of the reduction-oxidation furnace are close temperature control, a good heat-transfer system, and close control of the furnace atmosphere. Previous magnetic operations in which hearth furnaces, rotary kilns, and shaft furnaces had

been used indicated that the only type of furnace which met these requirements was a shaft-type unit. It was this type of furnace which was constructed for the pilot plant work. Two features, not normally a part of a shaft furnace, were required. These were a bypass system for passing heat-transfer gases around the reduction zone, and an external line for recycling the heat-transfer gas.

The comparatively low temperature of 930°F used in the reduction-oxidation process made it feasible to construct the furnace of metal rather than refractories. For the highest temperature zones, the reduction zone with a reducing atmosphere, and the oxidizing zone with an oxidizing atmosphere, an 18-8 type stainless steel was chosen. For the remainder of the furnace, regular cold rolled steel was used. Because of the small size of the pilot plant furnace with its resultant high surface to volume ratio, it was necessary to use a heavy coat of insulation to reduce radiation losses to a minimum. Vermiculite was chosen for insulation because of its stability over the desired temperature ranges.

Fig. 2 is a drawing of the furnace. This unit, which was designed for operation with a feed rate of 200 lb of raw ore per hr, consists of a stainless steel tube 2 ft in diam and 22 ft in length. This tube is surrounded by 2½ ft of vermiculite insulation, held in place by a second shell of lightweight aluminum sheet mounted on a structural-steel frame.

The furnace is charged and discharged by screw feeders. The reducing gas enters the furnace through annular manifolds, while the air for oxidation enters the furnace through a series of air inlet pipes.

In order to conserve heat and at the same time take advantage of the better heat-transfer properties of water vapor, as compared with air, a bypass line returns water vapor from the top of the furnace to the bottom section of the furnace where it is reused as a heat-transfer medium. To maintain a high hydrogen concentration in the reduction zone, a bypass manifold was installed to allow the heat-transfer gases, composed of water vapor and nitrogen, to travel around the reduction zone, thus avoiding dilution of the hydrogen used for reduction.

Burners located in the central and lower sections of the furnace are used to bring the furnace charge to reaction temperature before starting the cyclic-heat operation. The exhaust line at the top of the furnace removes the excess steam from the drying operation and the gaseous reaction products formed in the reduction zone.

In normal operation, the ore is fed into the top or preheating zone where heat from the furnace gases dries and preheats the ore. The dry preheated ore then passes into the reduction zone, where contact with a reducing gas converts the hematite to a magnetite. The reduced ore in turn passes into the oxidation zone where air converts the artificial magnetite to gamma hematite and releases heat. At the same time, the water vapor entering the bottom of the furnace serves as a heat-transfer medium, abstracting both the sensible heat from the ore and the heat produced by the oxidation reaction. The heated water vapor is then used to preheat and dry more ore, resulting in a cyclic process as regards heat requirements.

A stationary slotted cone was installed under the screw feeder to assure the distribution of fine ore across the diameter of the furnace. Fig. 2 shows the furnace substantially as it was employed for the test program on the processing of low grade taconites. The only exception was the substitution of a revolving chute for the stationary slotted cone in tests where feed contained over 20 pct of −10 mesh ore.

Pilot Plant Test Data

In the initial test work with the pilot plant furnace, pure hydrogen was used as the reducing gas. Later in the program the furnace was operated with producer gas.

The original tests were carried out with a feed consisting of an oxidized taconite having the following pct composition: Total Fe, 33.2; Fe,'' 3.1; Acid-soluble Fe, 33.1; Magnetic Fe, 10.1; Nonmagnetic Fe, 23.1; SiO_2, 51.3; CaO, 0.01; MgO, 0.08; and Al_2O_3, 0.13. In this ore, approximately two thirds of the iron was present as hematite and one third as magnetite. The gangue was primarily silica. At a later date, other ores containing varying amounts of hematite, magnetite, and siderite were processed

At the start of the pilot plant work, the furnace feed consisted of −½-in. + 10 mesh ore. In subsequent tests, −1-in. × 0 ore was employed. Some of the data collected in this test work will be discussed here. The purpose of the initial tests made with the pilot plant furnace was to prove that the fundamental concepts of the reduction-oxidation

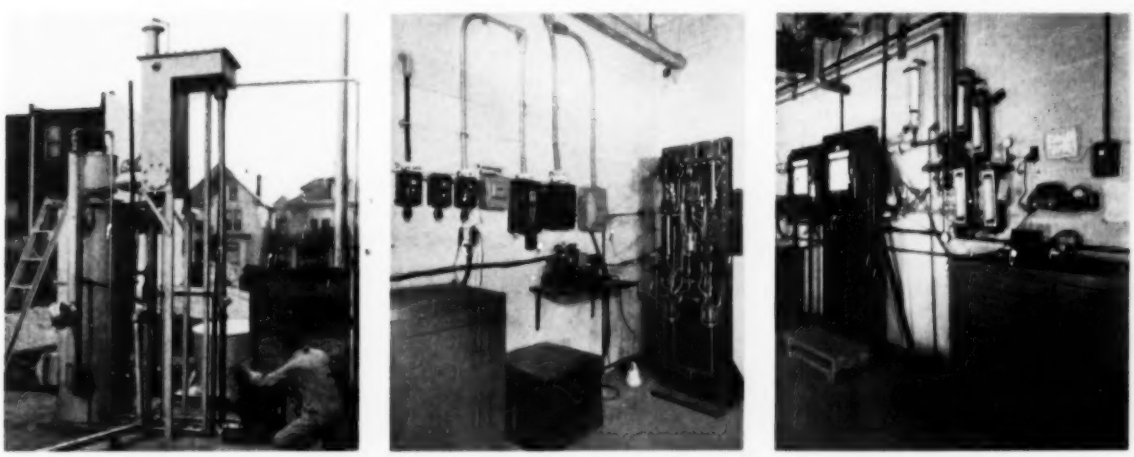

Fig. 3—The Wellman gas producer, shown at left, Cambridge gas analyzer, center, and the automatic temperature and gas recorder, right, were added to the pilot plant furnace before tests were made on the use of producer gas in place of pure hydrogen.

Table III. Magnetic Separation Tests on Samples From the Pilot Plant Reduction-Oxidation Furnace Operating With Hydrogen, Pct

Sample No.	Feed Fe	Magnetic			Nonmagnetic		
		Weight	Assay Fe	Dist. Fe	Weight	Assay Fe	Dist. Fe
1	36.7	58.71	60.9	96.68	41.29	3.0	3.32
3	36.4	58.70	60.5	96.41	41.30	3.2	3.59
5	36.4	55.64	60.9	93.51	44.36	5.3	6.49
7	36.5	52.27	62.1	87.18	47.73	10.0	12.82
9	36.3	52.68	61.6	89.09	47.32	8.4	10.91
11	36.4	53.50	61.6	89.86	46.50	8.0	10.14
13	36.0	55.16	61.3	93.09	44.84	5.6	6.91
Average 1 to 13	36.4	55.2	61.3	92.3	44.8	6.2	7.7

Table IV. Average Values For Various Feed Rates, Pct

Feed Rate, Lb per Hr	Recovery Fe	Assay Fe
200	96.3	63.9
400	94.9	63.6
600	94.2	63.9

Table V. Influence of —10 Mesh on Reduction-Oxidation Furnace

—10 Mesh in Feed Ore	Character of Furnace Operation
30	Noncyclic
23	Semicyclic
10	Cyclic
0	Cyclic

process were technically feasible. In these tests, tank hydrogen was employed as the reducing gas. A measured flow of two times the theoretical volume of hydrogen required to convert hematite was passed into the reduction zone of the furnace.

There are two methods of preventing the overreduction of iron in any reduction process. The first is based on adjusting the composition of the reducing gas so that the stable form of iron in such an atmosphere is magnetite. For example, at a reduction temperature of 750°F, a gas containing from 1 to 80 pct hydrogen and 20 to 99 pct water vapor will reduce Fe_2O_3 to Fe_3O_4 but will not reduce Fe_3O_4 to metallic iron. The second method of preventing overreduction is to limit the amount of reducing gas used, because it requires nine times as much hydrogen to reduce Fe_2O_3 to Fe as is required to reduce Fe_2O_3 to Fe_3O_4. By using twice the theoretical amount of hydrogen required to produce Fe_3O_4, it is possible to take advantage of both of these methods of preventing overreduction. On one hand there is insufficient reducing agent to form large amounts of metallic iron, and on the other hand, as the hydrogen is consumed in producing Fe_3O_4, the reaction product, water, automatically adjusts the composition of the remaining gas to a point where only Fe_3O_4 is stable.

In these initial tests, the pilot plant furnace was operated successfully on a cyclic-heat basis for periods as long as 80 hr, and made a high grade product. Table III gives typical data obtained from these tests and shows that during the test an average of 92.3 pct of the iron was converted to a form which could be recovered in a magnetic concentrate assaying 61.3 pct of iron. The results proved that the fundamental principles of the process were technically sound. These tests also showed that the amount of heat liberated by the oxidation of artificial magnetite to gamma hematite was more than sufficient to preheat the raw ore and sustain the reduction reaction, thus allowing the furnace to operate on a cyclic-heat basis.

After demonstrating the fundamental soundness of the process in tests with pure hydrogen, it was decided that tests should be made with other reducing gases. In considering other possible gases which might be used, it was apparent that most of the available gases had compositions intermediate between producer gas and pure hydrogen. Because of this, the decision was reached to test the process with producer gas on the assumption that, if the process worked with pure hydrogen and with producer gas, it would be operable with any of the intermediate gases such as reformed natural gas or water gas. Following these decisions, the pilot plant furnace was equipped with a gas producer and automatic gas analyzer as shown in Fig. 3. A series of tests was made, after adding this equipment, to show the workability of the reduction-oxidation process when operated with producer gas as a reducing agent. The performance of the furnace, when operated with producer gas, was comparable to its previous performance with hydrogen.

Although the 2-ft diam furnace was designed for a capacity of 200 lb per hr, the test data indicated that it was capable of processing ore at much higher rates. On this basis, a capacity test was made while operating the furnace on producer gas. In this test, the furnace was placed in operation at a feed rate of 200 lb per hr with a —½ in. feed containing 6 pct —10 mesh material and held at this rate until the temperatures in the various zones of the furnace reached their proper values and the furnace was operating on a cyclic-heat basis. The feed rate was then continued at 200 lb until the original charge was completely replaced with fresh ore. The feed rate was then increased to 400 lb per hr and maintained at this rate for a period of 24 hr, at the end of which it was increased to 600 lb per hr. The furnace was then operated at 600 lb per hr for 16 hr.

The average result for the entire run was a recovery of 95 pct of the iron at a grade of 63 pct of iron. Table IV is a summary of the data for the average values for the various feed rates.

These results show that producer gas is a satisfactory reducing agent for the reduction-oxidation process and that the process is capable of relatively high capacities per unit area of furnace.

Such variables as the size consist of the feed, the distribution of the various sizes in the furnace, and the distribution of the gases are major factors influencing the transfer of heat throughout the furnace. The initial tests with the furnace confirmed the influence of these factors, and it was decided to determine quantitatively, if possible, the effect of the screen size composition of the ore on heat transfer in the furnace.

Furnace tests were made with feeds containing varying amounts of —10 mesh ore. It was realized that more than likely the —65 mesh ore was the cause of poor gas solid contact. However, to facilitate the screening operation, the separation was made at 10 mesh. Table V shows the influence of —10 mesh ore on the operation of the reduction-oxidation furnace.

The data show that the reduction-oxidation furnace was readily operated on a cyclic-heat basis with a feed containing less than 20 pct —10 mesh ore.

The test program was next expanded to develop

a means of treating the ore without removing any of the fines. Two methods of handling the fines problem were investigated. First, a series of tests was run which showed that ore as coarse as 1 in. could be reduced within the retention time obtainable in the pilot plant furnace. By treating coarser ore, the amount of −10 mesh material produced by crushing a soft ore was reduced from 40 to about 25 pct of the weight. Second, a study was made in a replica of the reduction-oxidation furnace to ascertain the effect of distribution of the ore, by selective feeding, on the flow of the heat-transfer gases through the broken solids. Tests in the replica were carried out on ores containing as much as 25 pct −10 mesh material. These studies indicated that, by feeding the ore around the periphery of the furnace, sufficient gas-solid contact might be obtained to operate the furnace on a cyclic-heat basis.

Based on the knowledge obtained from the replica, a revolving chute was installed in the pilot plant reduction-oxidation furnace to distribute the feed around the periphery of the furnace.

To prevent the heat transfer gases from penetrating the reduction zone, a 3-in. bypass pipe was installed vertically in the center of the reduction zone. With the pilot plant furnace modified in this manner and treating a 1-in. feed containing 25 pct of −10-mesh material, tests showed that the furnace could be operated on a cyclic-heat basis at feed rates up to 400 lb per hr. At a feed rate of 600 lb per hr, the ore moved through the preheat zone at too fast a rate to permit the fines around the periphery of the furnace to absorb sufficient heat from the adjacent coarse ore to maintain a satisfactory operation.

Although peripheral feeding was employed in these tests, it was used only to distribute the heat-transfer gases, by distributing the ore, to obtain sufficient gas-solids contact to maintain the proper temperatures in the preheat zone. It is believed that in a larger commercial furnace the transfer of heat from the oxidation zone to the preheat zone, to permit operation on a cyclic-heat basis, is a matter of obtaining the proper relation between the distribution of the reducing and heat-transfer gases and the distribution of the ore. The specific method of feeding is not important so long as the ore is distributed in such a manner that adequate gas-solids contact is obtained to heat the ore.

The experimental work with the reduction-oxidation process for recovery of iron from the low grade ores of the Mesabi Range has shown that the mineral composition of the ore must be considered in determining the optimum conditions for operating the furnace. Because one of the requirements of the process is the oxidation of artificial magnetite to gamma hematite to supply heat for the process, the ore must contain at least 20 pct of the total weight as iron in the form of Fe_2O_3. To oxidize any natural magnetite present in the ores at a reasonable rate, the temperature must be greater than 1000°F, and at this temperature part of the iron values would be converted to nonmagnetic alpha hematite. For this reason, in the reduction-oxidation process, the natural magnetite contributes little if any heat for maintaining the process on a cyclic-heat basis. However, because the natural magnetite can be recovered with the magnetic gamma hematite by wet magnetic-concentration methods, the presence of natural magnetite does not interfere with the furnace operation if sufficient iron is available in the form of Fe_2O_3 to maintain a cyclic-heat operation.

Work with an ore that contained iron in the form of siderite as well as hematite showed that it was possible to convert to magnetite or to reject, as unaltered siderite, up to 75 pct of the original siderite in the ore by choice of operating temperatures in the reduction zone of the reduction-oxidation furnace.

In general, the experimental work has shown that the reduction-oxidation process can be adapted to the treatment of ores of wide mineral composition.

Summary

A new process has been developed for the treatment of oxidized taconites. The reduction-oxidation process combines a low temperature gaseous-reduction step and a controlled reoxidation step with a direct-heat-transfer system to give a process which requires no external heat.

The controlled reoxidation reaction is highly exothermic and produces gamma hematite as an end material. Gamma hematite, which is in metastable equilibrium, has the chemical composition of hematite, Fe_2O_3, but retains the cubic crystal structure and magnetic properties of magnetite, thus making it feasible to separate the iron values from the gangue by normal magnetic-separation procedures.

The operation of a 2 ft-diam shaft furnace at feed rates of up to 600 lb per hr has definitely shown that the process is technically feasible. Tests with this furnace have also shown that the process is applicable to a wide variety of taconites, including mixtures of hematite, magnetite, and siderite.

The high recovery of iron units, 92 to 96 pct, in magnetic form from ores treated by this process, plus the increased grindability of the processed ore, indicate that the method will be economically attractive. Where other processes require three or more tons of ore for the production of one ton of concentrates, the reduction-oxidation process needs only two tons and the fine grinding costs are decreased by two thirds. The savings in mining and grinding costs should more than offset the cost of roasting the ore by the new process.

Acknowledgments

The development of the reduction-oxidation process was one part of an overall research project on the development of concentrating processes for Mesabi taconites. This project was sponsored at Battelle by a group of producing iron ore companies and was active during the years of 1942 through 1952. The individual companies cooperating in this sponsorship were:

Armco Steel Corp.
Battelle Memorial Institute
Cleveland Cliffs Iron Co.
M. A. Hanna Co.
Inland Steel Co.
Jones & Laughlin Steel Corp.
Oglebay, Norton & Co.
Oliver Iron Mining Div., U. S. Steel Corp.
Pickands Mather & Co.
Republic Steel Corp.
Snyder Mining Co.

The authors wish to express their appreciation to these iron ore companies, who have kindly permitted use of the data given in this paper. Special appreciation is due the technical committee and the sampling committee members of the iron ore companies for their active cooperation in developing the process.

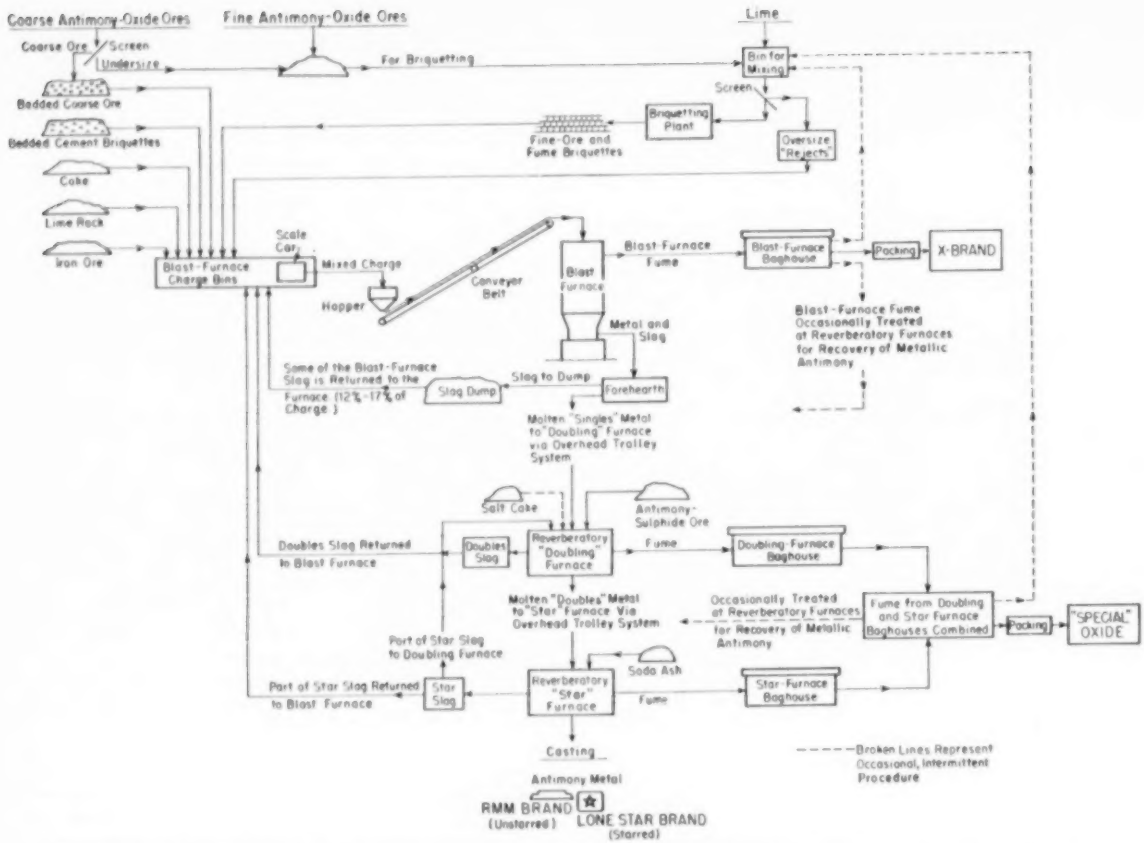

Fig. 1—Laredo smelter receives antimony-oxide ores from subsidiary interests and outside purchases, and produces metal that analyzes 99.5 to 99.8 pct Sb. As shown on the flowsheet, the use of the blast furnace for medium grade oxide ores and low grade sulphide ores, followed by refining in reverberatory furnaces, is standard practice at Laredo.

Mechanization Program Results In Savings at Laredo Antimony Smelter

by R. L. Kulpaca and J. C. Archibald, Jr.

THE National Lead Co. smelter at Laredo, Texas, smelts custom antimony ores for the production of metal whose purity varies between 99.5 pct and 99.8 pct Sb with no single impurity exceeding 0.10 pct. Occasionally, metal is produced containing up to 0.20 pct lead, but normally, strict limitations are placed on the lead content of the ores to be smelted. Other objectionable impurities that must be limited are arsenic, bismuth, copper, tin, zinc and selenium, so that refining costs do not become excessive. The precious metal content of the ores is usually so low that no attempt is made to recover those values.

Ores are received principally from subsidiary mining interests in Mexico, although purchases of ores from Idaho, California, Nevada, and Arizona are common. The flowsheet for normal treatment of ores is shown in Fig. 1.

The use of the blast furnace for medium grade oxide ores and low grade sulphide ores, followed by refining in reverberatory furnaces, is standard practice in Laredo. Other than a brief description of the furnaces, no other details of the smelting operation will be given, since the intent is to describe several improvements that have been made in the handling of the products, and consequent cost reduction.

Blast Furnaces: The blast furnaces, of which there are three, are similar to those commonly used for smelting lead. They are, however, slightly smaller than the usual lead blast furnaces. The rectangular shaft is 18½ ft high, constructed of common building brick on the outside, with the inside lining of firebrick. The water jackets reach from the top of the pedestal to the arches of the shaft, a distance of 5½ ft. Eight tuyeres are provided on each side of the furnace. Slag and metal are tapped into a small forehearth and the metal is drawn from this forehearth at intervals. Fig. 2 shows impure antimony metal being drawn from the blast furnace forehearth.

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Fig. 2—Slag and metal are tapped from the blast furnace into a small forehearth. Impure antimony metal is shown being drawn from the furnace forehearth for transfer to refining furnaces.

Refinery Furnaces: The crucible-type reverberatory furnaces are gas-fired. There are three of them with a capacity for batch treatment of 12,000 lb of metal in the first refinery steps. Two smaller gas-fired reverberatory furnaces with capacities of up to 10,000 lb of metal are used in the final refining step. The fumes and flue dusts of all furnaces are collected in the baghouses.

General: The improvements were made over a period of years under earlier management, and began, in some cases, as early as 1947. The most recent improvement, providing for hot metal handling, was objected to because of a fear that control of the process would be jeopardized and metallurgical results would suffer. Nevertheless, the management at that time did sufficient testing to assure themselves of good metallurgical results. Other improvements, consist mainly in mechanization.

Hot Metal Handling

An overhead monorail system with electrically driven hoists recently installed permits transfer of the molten metal from furnace to furnace. This eliminated the old method in which the metal tapped from a furnace was cast, cooled, broken by hand into smaller pieces, and then charged cold into the next furnace. Besides saving labor, the monorail system saved time and fuel in the refining process, since it is not necessary to wait for the charge to melt before deslagging and fluxing.

Primary objection to the hot metal handling proposal was that there would be insufficient time for the assays necessary before refining. However, in actual plant tests, it was found that by standardizing the amount of fluxing and refining agents for each charge, and depending to some extent upon visual control, the necessity for *in-process* assays was eliminated.

The preliminary tests involved the use of a fork-lift truck for transporting the metal in a small ladle from furnace to furnace. This practice proved so successful that it was employed continuously until the monorail was finally installed. The layout of the monorail system is shown in Fig. 3.

The monorails and switches were suspended from existing trusses of the blast furnace and refinery buildings. A view of the monorail layout in the refinery building is shown in Fig. 4. For additional support, A-frames and wide flange-columns were erected and, in some cases, the monorail was capped with angle iron and rails to prevent excessive deflection under load where the unsupported span was

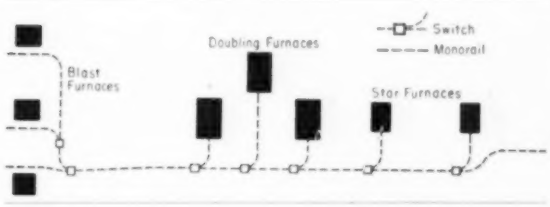

Fig. 3. Above—This is the layout of the overhead monorail system installed to permit efficient handling of molten metal from furnace to furnace.

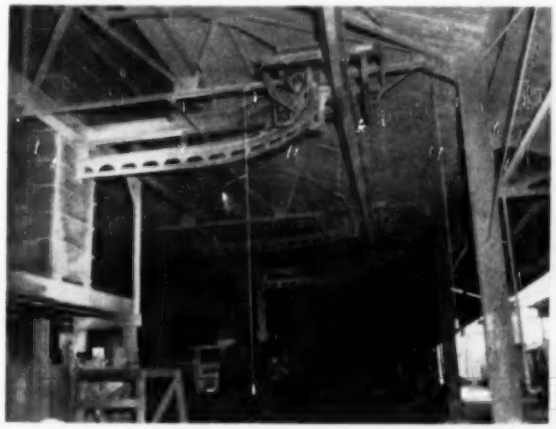

Fig. 4. Right—Selective switch arrangement for the furnaces can be seen in this view of the monorail layout in the refinery building.

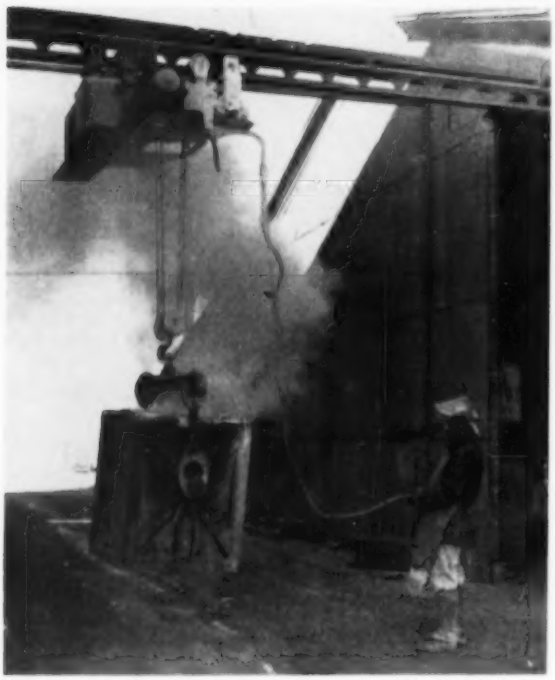

Fig. 5—Ladles of molten metal are transported from blast furnaces to refining furnaces with the electric hoist on arch beam monorail.

greatest. Three electrically operated hoists of 6000 lb rated capacity may be operated simultaneously on the monorail. One of the hoists transporting molten metal from the blast furnaces to refining furnaces can be seen in Fig. 5.

The hoists operating on 220 v - 3 phase power are also equipped with a motor for lateral movement, and are controlled through a pendant type push-button station carried by the operator.

The hot metal is transferred from furnace to furnace in ladles with capacities of 3500 lb. It was necessary to dig pits at the blast furnaces and doubling furnaces to accommodate the ladles.

After the final refining step the metal is tapped into a pouring ladle which is carried on the same monorail system to the molds. The ladle can be tilted for manual pouring, as shown in Fig. 6, or by an attached electric motor.

Fig. 6—Refined metal is poured into water-cooled molds. The ladle can be tilted by hand or by electric motor.

Since installation of this system, it has been possible to reduce labor by two men per shift on the three blast furnaces. At the refining furnaces, the crew was reduced by two men per shift, making a total of four men each shift, or twelve men a day. It is also pointed out that the efficiency of the operation was increased since the average production at the refinery increased from 1.66 tons per man-shift to 1.86 tons per man-shift. It is believed that after the men have become accustomed to the new system, the production rate will increase to 2.25, or even 2.50 tons a man-shift.

Water-Cooled Molds

When the monorail system was installed, water-cooled molds were added for casting finished metal. Two benches of 20 molds each were purchased. In conjunction with installation it was necessary to construct a water tank with cooling tower. These water-cooled molds do not reduce the amount of labor during the casting, but do improve the appearance of the pigs cast in these molds.

Ore Bedding With Tractor: An older innovation, but nevertheless a labor saving one, was installed several years ago when an International T-9 tractor-dozer was purchased for use, among other things, in bedding the ore.

It has been the practice at the smelter, as ores come from different mining districts, that they be bedded in beds up to 600 tons, permitting a uniform charge over an extended period of time in a blast furnace run. The bedding was accomplished previously by spreading each car of ore over the entire width of the bed, amounting to approximately 1800 sq ft, by hand labor. Now, with the tractor, this can be accomplished in about 1 hr.

Breaking Slag: One of the important losses that can occur is the metal buttons in slag. Normally, these buttons will sink to the bottom of the slag. It has been a practice to allow a crust to form in each slag-pot before pouring and then to pour all of the liquid slag from the slag-pot, leaving only that portion of the slag which might be expected to contain metallic buttons. The crust is then dumped from the slag-pots in another location, and broken up for recharging to the blast furnaces.

The work was originally done by hand, but several years ago a P&H crane was purchased. The crane has been used with a great deal of success in breaking up the slag for recharging.

Blast Furnace Baghouse Clean-Out Doors: It was formerly the practice to remove the flue dust from the blast furnace baghouses through small clean-out doors, using a long handled rake to drag the flue dust to the outside. The flue dust was shoveled into wheelbarrows and weighed on a small scale.

The cleanout doors were enlarged and the floor of the chambers deepened to accommodate a small carscoop. The carscoop is capable of handling the clean-out job in much less time than by the old system. Weighing is now done by Payloaders after all of the flue dust has been taken from the baghouse.

Conclusion

The results obtained thus far with mechanization of work formerly done by hand indicate that replacement of manual labor by equipment returned a substantial saving. Other savings will be realized through expansion of this mechanization program.

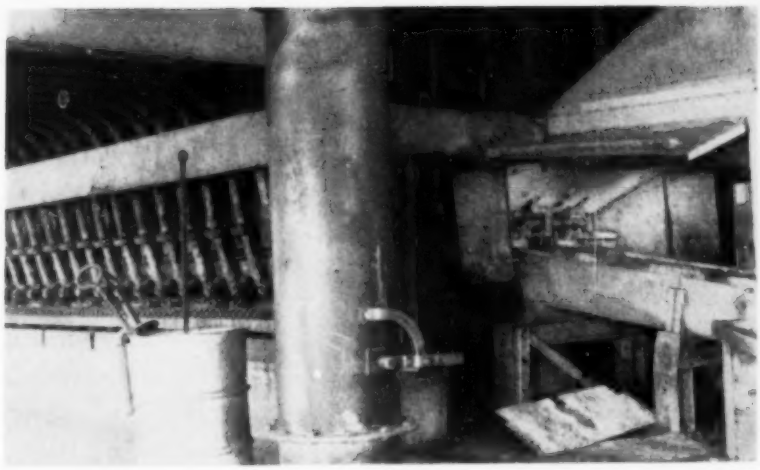

Fig. 1—The slag fuming furnace, built at the Chihuahua smelter where large tonnages of dump slag containing better than 10 pct Zn were available, is completely water jacketed, with the usual 21 double-inlet tuyeres on each side. Furnace charge consists of 45 tons of slag.

Chihuahua Slag Fuming Plant To Process 19,000 Tons Per Month

by V. R. MacDonald

DECISION to build a slag fuming plant at the Chihuahua smelter in August 1950 was based on availability of large tonnages of dump slag containing 10 pct zinc or better. Slag derived from operations also reached or bettered the standard.

A contract was signed with Utah Construction Co., in February 1951 and work began immediately. The plant was completed in July 1952. It was built on a vacant site northwest of the lead smelter and at the base of the slag dump. The location proved ideal because of lack of obstructions. The result was a compact plant with straight-line gas flow permitting automatic furnace and kiln draft maintenance within close limits, and dust has to be cleaned out of the system only on the day shift.

Hot slag is weighed in 300 cu ft ladles, delivered into a 70-ft craneway, and poured into a standard 8x21x33-ft furnace. The furnace, Fig. 1, is completely water-jacketed with the usual 21 double-inlet tuyeres on each side. The tuyere piping, 1-in. thick hydraulic tubing of 1⅛ in. ID, is 5½ in. above the bottom jackets, extending 10 in. into the furnace. After practice developed at El Paso, 2 in. studs were welded to the face of the tuyere jackets on 1½ in. centers. A few hours after starting up the plant a smooth and protective 2 in. coating of slag was deposited around the studs.

The cross-over flue and inclined flue leading to the brick spray chamber also are completely water-jacketed, with cooling water controlled by a thermo-syphon system. The brick spray chamber was found necessary because there is no waste heat boiler in the system. It discharges gases into a 7-ft diam balloon flue 93 ft long, then into the U-tube coolers illustrated by Fig. 2, and to the baghouse. There is a second spray chamber when additional cooling is necessary. Both spray chambers have automatically controlled air inlet dampers keeping water cooling to a minimum.

There are four banks of U-tubes each 3 ft diam and 48 ft high, 20 to a bank. Gases are delivered into the baghouse by two American Blower Co. No. 22 Type SE fans running in parallel. Each fan delivers 87,500 cfm and has automatically controlled inlet doors for furnace draft control.

The baghouse is constructed of locally manufactured red brick and consists of eight sections, each containing 126 standard 18 in. x 30 ft woolen fume bags. Dust that accumulates under the balloon flue and U-tubes is collected on day shift by drag conveyors and delivered to a partitioned 250-ton storage bin. Baghouse cellars also are cleaned on day shift by a scraper, connected to a three-drum tugger, and delivered to the same storage bin, permitting a proportioned charge of the two kinds of dust to the deleading kilns.

An Ingersoll-Rand turbo-blower connected by a step-up gear to an eight cylinder, 800-hp IR diesel engine supplies air for the furnace. Rated capacity of the blower is 14,000 cfm at 12 lb. An automati-

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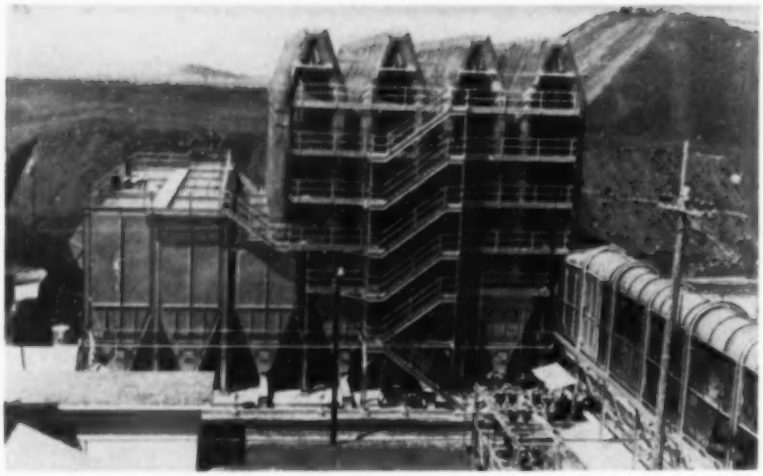

Fig. 2—As there is no waste heat boiler in the system, a brick spray chamber discharges gases into a balloon flue, then into the U-tube coolers shown, and to the baghouse. For additional cooling, a second spray chamber is provided after the U-tube coolers.

cally controlled butterfly damper divides the air into primary and secondary air. Primary air, 4400 cfm, is split between two B&W air heaters and then to two B&W Type E, Size 38, pulverizers, where it picks up the coal. Coal-air mixture is delivered to the primary inlets of the tuyeres. Secondary air goes directly to the tuyeres.

Velocity of primary air through the pulverizers controls coal flow to the furnace, which varies from 90 lb per min during the charging cycle, to 165 lb per min during the reducing cycle. Lower coal flow during the charging cycle permits complete combustion for maximum heating of the slag. Total air is held at 12,000 cfm. All operations pertaining to the fuming furnace are controlled from a room near the furnace containing a set of Bailey Meter Co. instruments.

Coal used is of the following analysis, dry basis: Volatile, 21.30 pct; free carbon, 72.15 pct; ash, 6.55 pct; and btu, 14,500. Coal is dumped into a track hopper and is belt conveyed to 24-in. corrugated rolls, then to a 300-ton storage bin or to a Redler conveyor feeding 30-ton bins over the pulverizers. Although the plant has been in operation only a short time, indications are that 19,000 short tons of slag will be processed monthly.

Heads are 12 pct zinc, with 2 pct zinc in the tails, for an elimination of 85 pct after shrinkage allowance. Charge to the furnace consists of three ladles of slag, equalling 45 tons. Blowing time is 90 min at 8.5 lb pressure. Gas leaves the furnace at 2300°F. After passing through the water jacket cross-over and inclined flue it is further cooled by the spray chamber and enters the U-tubes at 900°F and then in the baghouse at 225°F. Analysis of fume collected in the baghouse is: Zn, 67.0 pct; Pb, 8.0 pct; Cu, 0.10 pct; SiO_2, 0.9 pct; Fe, 0.8 pct; weight per cu ft, 30.0 lb. Flue system analysis is: Zn, 67.0 pct; Pb, 7.0 pct; Cu, 0.10 pct; SiO_2, 0.9 pct; Fe, 0.8 pct; weight per cu ft, 32.0 lb.

The two types of dust are blended with 2½ pct coal and fed to 75x7-ft rotary kilns. Kilns are oil fired and discharge temperature is maintained at 2350°F. Lead oxide fume is discharged into a hopper-bottom brick flue and then into U-tubes, 30 in. diam x 40 ft high, and into the lead baghouse shown in Fig. 3. An American Blower Co. Type SE fan of 45,000 cfm maintains draft in kilns and flue system.

The deleaded clinker is discharged into a 6-tube Traylor cooler. It then goes to a 300-ton storage bin, from where it is crushed and passed over a ¼-in. vibrating screen and loaded out to a zinc retort smelter. The deleaded product and lead-oxide fume caught in the baghouse have the following analysis: Deleaded product-Zn, 77.0 pct; Pb, 0.5 pct-Baghouse product, Zn, 20.0 pct; Pb, 52.0 pct.

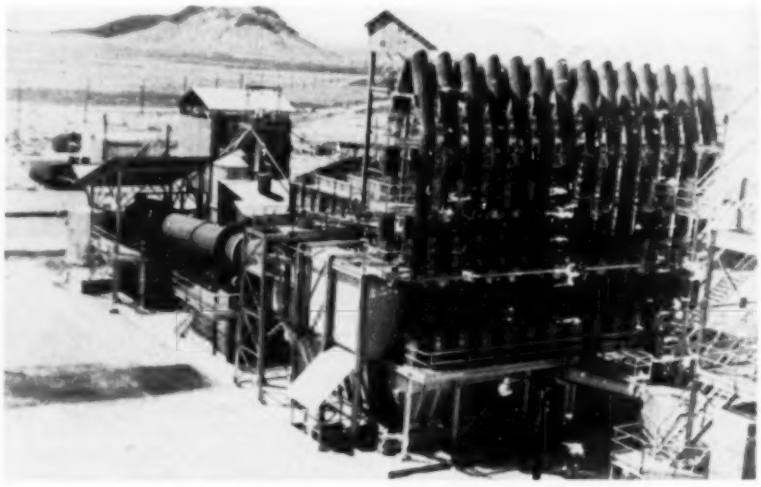

Fig. 3—Lead oxide fumes are discharged from the rotary kilns into a hopper-bottom brick flue, then into U-tubes, and then into the lead baghouse shown. A 45,000 cfm fan maintains draft in the kilns and flue system.

Fig. 1 — In this method, the time of returning a banked furnace to 80 pct normal blast has been reduced from about 72 to 30 hr. This view shows both the section of 4-in. pipe that forms the tapping hole and the ball joint.

Lorain Cuts Banked Blast Furnace Blowing-In Time From 72 To 30 Hours

by Walter W. Durfee

PRIOR to 1946, when returning a banked furnace to blast, the procedure at Lorain was to quarry the iron notch straight back to loose coke, make up the tapping hole with a piece of 4-in. pipe, brick up the cinder notch, and remove the main skimmer. With the four front tuyeres open, the furnace was blown with 20,000 cfm while an effort was made to keep the hole open by means of a pricking bar and an oxygen lance. The hole would invariably seal off before a run of hot slag was obtained. When the hole sealed off, the wind was advanced to 30,000 cfm. After 16 hr, a decision had to be made whether to open the tapping hole early and chance getting a free run of metal and slag, or to wait until a greater head had accumulated, and chance getting the hole. Hard clean-ups when the hole was opened early and failure to get the hole when the opening was delayed, led to the conclusion that there was no preferred choice. On a furnace that had been banked for a month, 80 pct of normal blast was not usually reached until three days after blowing-in. Reference is made to 80 pct of normal blast since the increase from 80 pct to 100 pct depends on the rate at which the steel works can consume hot metal and the ability of the railroad to move ladles in time to make short casts until the furnace is casting normally.

Since 1946, when returning a banked furnace to blast, Lorain has followed the practice of blowing into the iron notch. The same procedure is followed when blowing-in a furnace from which the salamander has not been removed. As formerly, the notch is quarried straight back to loose coke, the cinder notch is bricked up, the main skimmer removed, and the tapping hole made up with a 5-ft length of 4-in. pipe. One half of a ball joint was welded to the outer end of the pipe which is positioned so that the

WALTER W. DURFEE is Blast Furnace Superintendent, Lorain works, National Tube Div., U. S. Steel Corp. This paper was presented at the Blast Furnace, Coke Oven and Raw Materials Conference of AIME, Buffalo, Apr. 21, 1953.

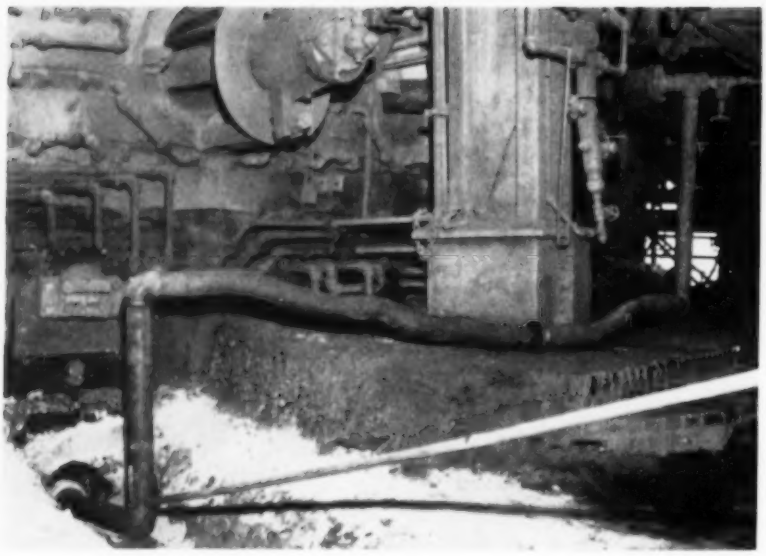

Fig. 2 — The assembly is in position for blowing into the tap hole. In this blowing-in method, the tapping hole substantially is converted into a tuyere. Flexible pipe in the assembly simplifies piping and facilitates withdrawal.

joint is flush with the face of the hole. An assembly of 4-in. pipe, starting with a special flange which replaces the peep-sight flange on the tuyere stock and terminating with the other half of the ball joint, is positioned and blocked in place. Included in the assembly are a 4-in. valve and a section of flexible steel pipe. The section of flexible pipe in the assembly greatly simplifies the piping and facilitates its withdrawal. Fig. 1 shows both the section of pipe which forms the tapping hole and the ball joint. Fig. 2 shows the assembly positioned for blowing into the tapping hole. The tuyeres are clayed-up, using clay only in those tuyeres where an early opening is anticipated. The others, including the one at which the blow-in pipe is located, have a brick wedged near the nose of the tuyere to offer more resistance to opening by the blast pressure. The blower is set to deliver 20,000 cfm, and the volume of blast entering the hole controlled by regulating the snorter to give a bustle-pipe pressure of 10 to 15 psi. When available, a blast temperature of 1100°F, as recorded in the bustle-pipe, has been used. After blowing into the hole for approximately 6 hr, the tuyeres in front of the furnace are opened, one at a time, and blast volume increased to hold the 10 to 15 psi blast pressure. Between 8 and 12 hr after starting to blow, the head of metal and slag in the furnace becomes sufficient to start a flow back into the 4-in. pipe. When this occurs, as indicated by color in the pipe, the blocking is removed, the pipe withdrawn, and the 4-in. valve closed. The withdrawal of the pipe is followed by a run of metal and slag, usually to the extent of only a stub ladle. The tapping hole is opened every 3 hr until the temperature of the slag warrants replacing the main skimmer.

Tuyeres are opened from the front to the back on each side of the furnace as fast as conditions warrant. When any slag in front of the tuyeres is observed to drain at cast time, the adjacent tuyeres are opened. Ability to get the tuyeres open early during the blow-in is a distinct advantage in obtaining uniform stock movement and getting the furnace on quality iron.

The outlined procedure, with some variation, has been followed on 12 occasions, on one of which it was necessary to make one cast through the cinder notch. Departure from the procedure consisted in admitting oxygen from the plant supply into the blast entering the tapping hole, or in blowing into the hole for a longer period before opening any tuyeres. A distinct benefit may be realized from the oxygen when starting with cold stoves. A higher temperature in the area of the iron notch appears to be associated with a longer blowing period before any tuyeres are opened. This higher temperature may be explained by the fact that although some blast continues to enter the tapping hole after tuyeres are opened, the volume entering the hole is considerably reduced.

Figs. 3, 4, 5, 6, and 7 illustrate the experience in returning the Lorain furnaces to blast following the 1952 steel strike. The furnace referred to in Fig. 7, which is normally blown with 90,000 cfm, did not reach 80 pct wind until 64 hr, whereas, the other four attained 80 pct of normal wind in 23 to 42 hours. The experience in bringing this furnace in from bank is reminiscent of blow-ins prior to the adoption of the described method and is attributed to the premature opening of a tuyere. Three hr after starting the blast into the tapping hole of this furnace, No. 2 tuyere was found to have opened itself and the volume of blast entering the tapping hole indicated it was sealing off. After the second attempt to get the tapping hole, the resulting mess in the trough warranted opening the bricked-up cinder notch. Following one cast out of the cinder notch, the tapping hole was obtained.

Summary

By following the described method, which is substantially converting the tapping hole into a tuyere, the time of returning a banked furnace to 80 pct normal blast has been reduced from approximately 72 to 30 hr.

Clean-ups are relatively light and are usually completed by the regular casthouse crews. Uniform stock movement is obtained earlier during the blow-in and the furnace is easier to control. Only one tuyere was burned during the blow-in of five furnaces in 1952. Hot metal, acceptable to the steel works, is obtained sooner, and fewer ladles are lost because of build-ups. The outlined procedure is covered by U. S. Patent No. 2,468,738.

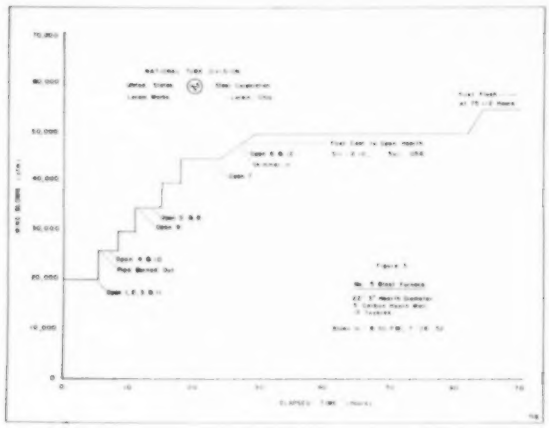

Fig. 3

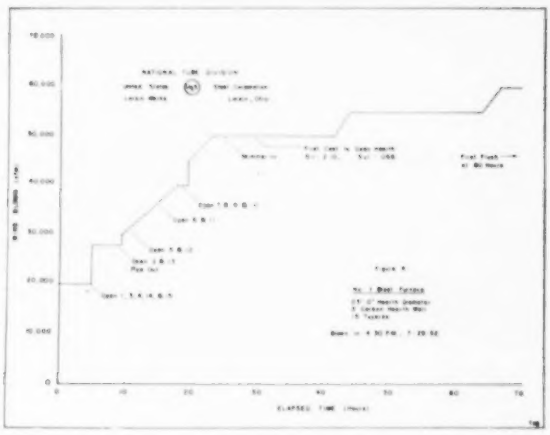

Fig. 4

Fig. 3 illustrates experience on blowing-in No. 5 blast furnace. Data for No. 1 furnace is given in Fig. 4, that for No. 2 furnace in Fig. 5, No. 3 furnace in Fig. 6, and No. 4 furnace in Fig. 7. All furnaces except No. 4 (Fig. 7) attained 80 pct of normal wind in 23 to 42 hr. No. 4 furnace took 64 hr, which was attributed to premature opening of a tuyere.

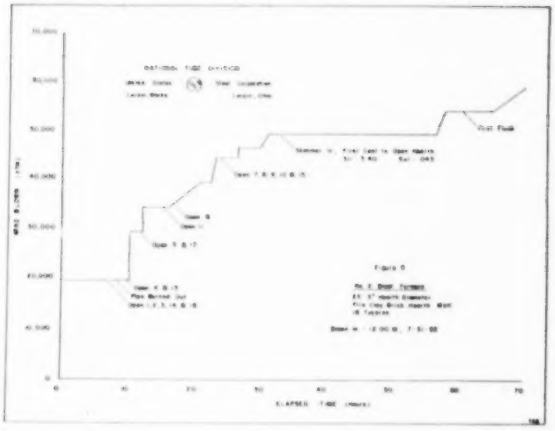

Fig. 5

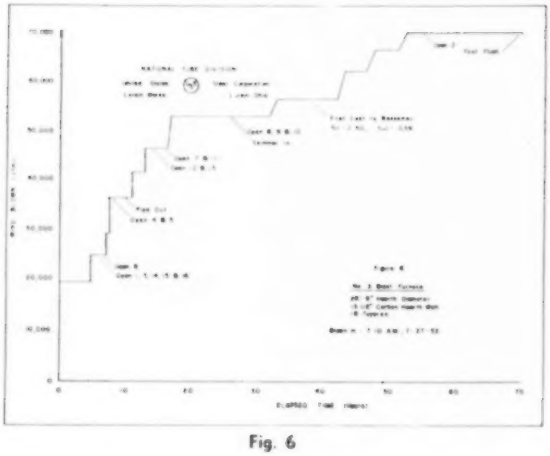

Fig. 6

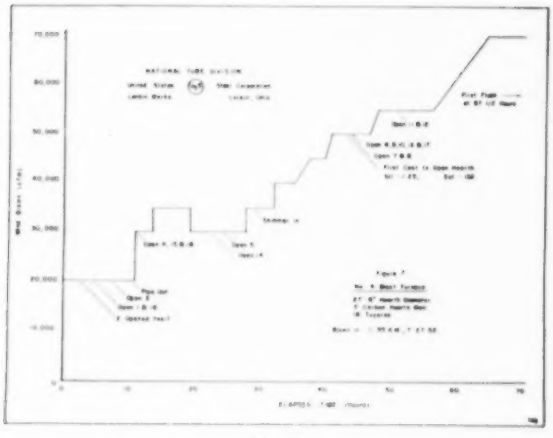

Fig. 7

Steam Jets Efficiently Remove Dust From Open Hearth Furnace Flues

by John Peterson

THE Midland works recently enlarged eight of its open hearth furnaces to 165-ton capacity. Included in the rebuilding program was a steam jet system for removing flue dust from flues underneath the checkers. This jet system has proved itself to be efficient in keeping regenerator flues from becoming clogged during a furnace campaign, as well as helpful in saving time on furnace cleanouts during rebuilds.

Each furnace was equipped with a series of steam jets in the regenerator flues and in a cleanout tunnel running the width of the checker chambers. Fig. 1 is an isometric drawing showing this steam jet arrangement. The checker chamber measures 23x25 ft, divided by rider walls into six flues. Each flue contains two steam jets facing the stack. One jet is located in the back wall of the flue 9 in. above the floor, the second is on the floor of the flue 9¾ ft in front of the first jet. The lower jet is bricked over to form a 6-in. step in the floor of the flue. Each pair of jets is controlled by one valve, a total of six control valves being required for each chamber.

The cleanout tunnel is located under the front of the checker chamber running perpendicular to the flues. The tunnel is 4 ft wide and 4 ft deep and contains three pairs of jets, arranged in 3-in. levels. The highest pair is located in the back wall of the tunnel, the second pair extends 9½ ft and the lowest pair 19 ft from the back of the tunnel. Each pair of jets is controlled by a separate valve, requiring three control valves for each tunnel.

The steam supply is taken from the main steam line at 175 lb pressure. Feed lines to the furnace are of 2½ in. extra heavy pipe. The steam nozzles are of stainless steel, 6 in. in length, with ¾ in. openings. Fig. 2 is a view of one of the regenerator flues showing the two steam jets. The brick covering over the lower jet had not been completed when this picture was taken. One flue is blown at a time to obtain maximum steam pressure. When the jets are turned on, the flue dust is blown towards the stack. Most of the dust settles in the cleanout tunnel, with some dust continuing on towards the stack to settle in the damper flues or to be carried out the stack.

Fig. 3 is a view taken in the cleanout tunnel, showing the arrangement of the three pair of steam jets. Again, the brick covering was not complete when the picture was taken. When the jets in the tunnel are operated, the dust is blown into a cleanout pit located between the checker chambers. Fig. 4 is a view taken from inside the cleanout pit showing the opening of the tunnel and the steel framed, brick-filled door which covers the opening when the furnace is in operation. The cleanout pit measures 15x10x16 ft, extending 2½ ft below the floor of the tunnel to permit depositing of the flue dust when the tunnels are blown.

JOHN PETERSON is Turn Foreman, Open Hearth, at the Midland works of Crucible Steel Co. of America. This paper was presented at the AIME National Open Hearth Steel Conference, Buffalo, Apr. 20, 1953.

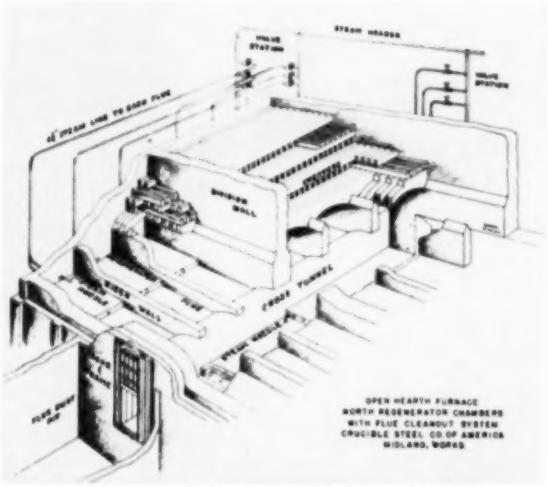

Fig. 1—The steam jet arrangement on one of the open hearth furnaces is shown in this isometric drawing on a plane through the rider walls.

Fig. 5 is a view of the area between the checker chambers showing the location of the cleanout pit. The pit is covered by steel plates which are removed when the flue dust is to be cleaned out. A small door can be opened for inspection purposes. A chain block is used to raise the doors when the tunnels are to be blown. A regular schedule is followed for keeping the regenerator flues clean. The flues are blown every five to seven days. One flue at a time is blown, on the end of the furnace drafting towards the stack. The steam is left on approximately 10

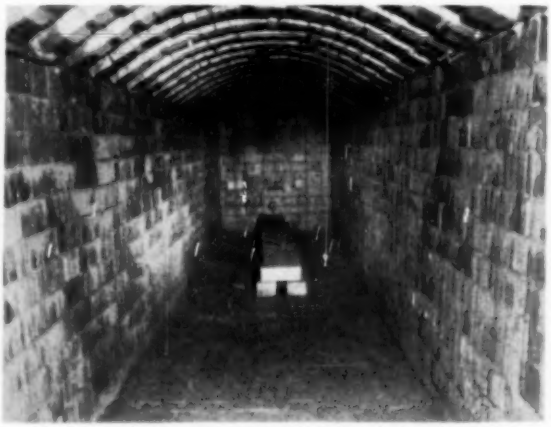

Fig. 2—Each flue contains two steam jets facing the stack. When this photograph of one of the regenerator flues showing the two jets was taken, the brick covering over the lower jet had not been completed.

min in each pair of jets. The cross tunnels are cleaned every third time the chamber flues are blown. The door is raised and the steam turned on in the pair of jets nearest the door for approximately 15 min, clearing the first section of the tunnel. The middle pair is opened for 15 min, then the rear pair for 15 min, clearing the middle and the rear sections of the tunnel. The middle and then the first pair are opened a second time to clear away the dust left when the rear sections were blown. The door is lowered and the operation repeated in the opposite checker chamber.

This steam jet blowing results in almost completely clearing the regenerator flues and cleanout tunnels. The dust is left in the cleanout pit until the end of the campaign, when it is removed by means of a vacuum system. Flexible pipes are attached to the vacuum line and extended into the pit to aid in removing the dust. The average campaign of these furnaces has been 425 heats, burning a combination of oils and coke gas, or pitch and coke gas, depending on the availability of the fuel. After approximately 225 heats a second roof is put on the furnace, which takes an average of 32 hr from gas off to gas on. There have been no instances where a light up after a quick roof has been delayed due to the necessity of cleaning clogged flues. At the end of the campaign there is no decrease in operating efficiency due to flue dust build up causing reduced draft in the passages under the checkers.

In a complete cleanout at the end of a campaign an average of 150 tons of solids are removed. Of this amount, up to 35 tons will have been deposited in the cleanout pit by the steam jet system. Both time and labor are saved by having the passages under the checkers cleaned out before the furnace is taken out of production at the end of the campaign. Ordinarily, the flue dust would have to be removed from under the hot checkers to make room for the additional solids deposited during checker scrapping operations. On these furnaces it is customary to start checker scrapping operations as soon as the chambers have cooled sufficiently to enter the air space above the checkers. The flue dust deposited in the cleanout pit during the campaign can easily and quickly be removed while waiting for the checkers to cool, or, as is more often done, left until the furnace cleanout has been completed.

Fig. 4—This view from inside the cleanout pit, shows the opening of the tunnel and the steel framed, brick-filled door which covers the opening when the furnace is in operation.

Summary

The steam jet system for removing flue dust, installed in the open hearth furnaces at the Midland works, has been successful in preventing flue dust buildup under the checkers. Delays caused by cleaning regenerator flues are avoided when the furnace is down for a second roof, and there is no decrease in operating efficiency near the end of the campaign due to reduced draft under the checkers.

Blowing the passages under the checkers while the furnace is in operation also saves time and labor on furnace cleanouts. The dust blown from under the checkers is deposited in a large pit where it is more accessible for removal, and checker cleaning operations can be started as soon as the chamber has cooled sufficiently.

Fig. 3—The cleanout tunnel, located under the front of the checker chamber running perpendicular to the flues contains three pairs of jets. As in Fig. 2, the brick covering had not yet been completed.

Fig. 5—The cleanout pit is located between checker chambers, and is covered by steel plates which are removed when flue dust is to be cleaned out. A small door can be opened for inspection of the pit.

Open Hearth Screw Steels Replacing Bessemer

by S. Feigenbaum

FOR many years the manufacture of added sulphur free machining steels for automatic screw machine use was confined largely to the acid bessemer process. Inherently high phosphorus and nitrogen contents of conventional bessemer steel, and the excellent machinability of the bar products rolled from these grades were factors favoring the continued production of bessemer screw grades.

During recent years, however, various economic and metallurgical considerations resulted in the broad expansion of open hearth steelmaking capacity and the gradual decline and abandonment of a significant proportion of the bessemer capacity in the U. S. Concurrently attention has been directed toward the possibility of producing steels equal or superior to the bessemer screw grades B-1111, B-1112 and B-1113 in the basic open hearth, and in occasional instances even in the electric furnace. One consequence of this activity was the formulation of a new series of standard steels, designated in the AISI manuals as C-1211, C-1212, and C-1213. These steels are analogous to the bessemer grades and are made to the chemical specifications shown in Table I.

Some producers have developed modifications of these basic compositions, to obtain further improvement in metallurgical characteristics.

Some time ago Jones & Laughlin Steel Corp. initiated experimental production of open hearth free machining grades in the research laboratory 4-ton open hearth furnace and in small open hearth furnaces in the plant. Representative tonnages of cold drawn bars were shipped to customers' plants and the performance in screw machine operation carefully evaluated. Favorable trade reactions were obtained and production of open hearth screw steel grades was undertaken on a broad scale.

From the standpoint of metallurgical practice it is entirely feasible to reproduce the bessemer range of analyses in the open hearth furnace. The nitrogen content may be duplicated consistently or varied over a fairly wide range, as desired, with the use of suitable addition agents. From the operating viewpoint, however, the change to open hearth practice introduced several problems that did not previously exist in acid converter practice. Among these were:

1—In the bessemer process it was possible and frequently desirable to introduce sulphur and occasionally some phosphorus with the converter charge, since acid slag has no effect on either of these elements. In the basic open hearth these additions must be confined to the ladle.

2—Phosphorus and nitrogen contents that are inherent in acid bottom-blown converter operation must be obtained from ladle additions in open hearth practice.

3—Large heats and correspondingly large additions required in the open hearth process presented physical difficulties that were previously of minor concern with small bessemer blows.

4—The low bath carbon content needed to make these grades was simpler to attain in the converter.

Table I. Chemical Specifications of C1211, C1212, and C1213 Steels, Pct

	Carbon	Manganese	Phosphorus	Sulphur
C-1211	0.13 max	0.60 to 0.90	0.07 to 0.12	0.08 to 0.15
C-1212	0.13 max	0.70 to 1.00	0.07 to 0.12	0.16 to 0.23
C-1213	0.13 max	0.70 to 1.00	0.07 to 0.12	0.24 to 0.33

Pittsburgh Works div. ordinarily produces the basic C-1200 series of steels in open hearth furnace of 225 net tons capacity. The practice established for these grades is briefly the following:

Furnace—Straight ferromanganese is added to meet specification split between standard and medium grades as indicated by requirements of the particular heat. Preferred bath temperature before manganese addition is 2910° to 2940°F. The heat is tapped approximately 5 min after the manganese is added.

Ladle—Flowers of sulphur and ferrophosphorus are added to meet the specification for these elements. If desired, nitrogen may be added in controlled amounts in any of several available forms. A small quantity of standard ferromanganese usually is added to make a final adjustment of analysis.

Molds—The steel is cast in 25x27 in. corrugated bottle top ingots, capped if necessary with a small quantity of crushed 90 pct ferrosilicon.

The practice described resulted in the production of steel that exhibits an excellent degree of uniformity within the heat and a high order of consistency from heat to heat. While a missed heat in the open hearth represents many times the tonnage of a bessemer blow, experience indicates that in the aggregate the C-1200 series has been less troublesome in that respect than the B-1100 group.

The surface quality of bessemer screw steels, particularly B-1113 grade always has been troublesome. The corresponding open hearth grades display somewhat similar hot rolling characteristics. In general experience indicates an appreciable superiority for the open hearth steels with respect to conditioning bed rejections and less extreme variation in quality from heat to heat. As the carbon content approaches the maximum of the specification, the hot rolling performance is adversely influenced. Manganese content over 0.80 pct is desirable and usually heats finish within the 0.80 to 1.00 pct range. Since tapping and teeming temperatures ordinarily may be controlled more closely in open hearth practice than in bessemer, it is reasonable to attribute some proportion of the improvement to this factor.

Thousands of tons of open hearth free machining steels have been made for a wide variety of applications and experience indicates that in ultimate use, the new grades are superior to the bessemer grades they have displaced.

S. FEIGENBAUM is Chief Metallurgist, Pittsburgh Works Div., Jones & Laughlin Steel Corp. This paper was presented at the National Open Hearth Conference, AIME, in Buffalo, Apr. 20, 1953.

The Influence of the Rate of Deformation on The Tensile Properties of Some Plain Carbon Sheet Steels

by Joseph Winlock

TO have been chosen by you to give the Howe Memorial Lecture is the greatest honor I have ever had and I should like to have you know that I appreciate it deeply.

Many years ago I had the privilege and the pleasure of working with Professor Howe in the private laboratory which he had established in his home at Bedford Hills, New York. Without doubt he was one of the world's greatest metallurgists and so you can imagine what a difficult task it has been for me to live up to his teachings.

Every morning Professor Howe would outline the work he wanted done and the recollections of those conferences are clear to me to this day. Sometimes he would ask me to ride in his automobile and the chauffeur had full instructions to go no more than fifteen miles an hour. If he did so, Professor Howe was sure to rap upon the man's shoulder with his cane. I assure you, however, Professor Howe's thinking was not at that rate. His homely advice, his patience and his perfect control of the English language still impress me. Many times I heard him dictate a complicated paper on metallurgy and never find it necessary to change a single word.

There are no better words to describe the character of Professor Howe, in my opinion, than those used by Professor Sauveur when he presented the John Fritz Medal to him in 1917:

> "Lover of justice and humanity
> Public servant and public benefactor,
> Master of the English Language,
> Loyal and devoted friend,
> Untiring and unselfish worker in an
> important field of science."

I hope you will bear with me with the same patience and understanding which he used to give to me.

The peculiar behavior of steel at the yield point has long been known and has been the subject of much research, both in this country and abroad.[1-5] Many theories, including some of mine and my colleagues, have been suggested, but none of them, in our opinion, fully explains to our satisfaction why the phenomena occur. Of particular importance has been the work of Nadai,[7] Siebel and Pomp,[4] Sachs and Fiek,[5] Rawdon,[6] Kenyon and Burns,[7] Gensamer,[8] Gensamer and Mehl,[9] Davenport and Bain,[10] Fell,[11] Deutler,[12] Brinkman,[13] MacGregor,[14] Hollomon,[15] Cottrell,[16] and Palm.[17]

The question of what is occurring during this singular behavior is not only of interest from an academic point of view, but is of great practical importance for at least two reasons: 1—The highly localized plastic flow which occurs during the deep drawing of light-gage steel gives rise to surface markings which seriously mar its appearance, Fig. 1. If the forces causing the deformation are primarily tensile forces, these surface markings occur as depressions in the surface. Whereas, if the forces causing the deformation are primarily compressive, irregular lines of elevations occur. These surface markings are known as Lüder's lines, Hartmann lines, the Piobert affect, and, in the shop, as "stretcher strains." 2—The steel is in the most suitable condition for deep drawing after the yield point phenomena have been removed. When this is done, the steel may be deep drawn more easily and to a greater extent.[1]

It should be mentioned that steel is not the only metal which shows this peculiar behavior at the yield point. Stretcher strains occur, also, during the deformation of some copper-nickel-zinc alloys.[18]

The purpose of this paper is not an attempt to describe what *causes* the steel to behave in this peculiar manner, but an attempt: 1—to describe *what* is taking place at the yield point; and 2—to show the influence of the rate of deformation on the tensile properties of some plain carbon steels.

As is well-known, there are two methods of deforming a metal in tension: 1—by actually hanging an increasing amount of dead weight on the metal; or 2--by deforming the metal at some given rate or rates by means of oil pressure cylinders, screws, etc. With the first method, the load is always present and, clearly, no drop in load can ever occur while the steel is deforming. With the second method, the registered load is the resistance of the steel to the deformation being imposed upon it. The second method is the one most widely used, and is the one referred to throughout this paper.

In order to describe clearly what is occurring at the yield point in steel, it will help, I believe, if a description is first given of what occurs when alumi-

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The Transactions papers appearing in the Journal of Metals during 1953 will subsequently appear in AIME Transactions Volume 197, and may be permanently referenced to that volume.

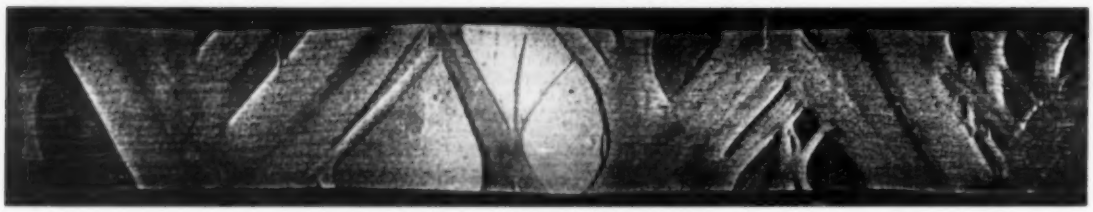


Fig. 1—Tensile specimen showing Luder's lines.

num and most other metals are elastically and plastically deformed in tension.

At the instant deformation begins, the aluminum begins to offer a resistance to deformation and for a certain distance the load-deformation curve rises as a substantially straight line. So long as the curve remains substantially straight, the deformation is substantially elastic. But, when the deformation becomes so great that the resistance of the metal to elastic deformation is overcome, plastic deformation takes place. This is shown in Fig. 2. It is to be noted, too, that the metal exhibits a continually increasing resistance to deformation until the maximum load is reached; and, of particular importance, is the fact that the curve is smooth from origin to fracture. That is, as the change from the substantially elastic state to the substantially plastic state takes place, the metal immediately offers a greater resistance to deformation and, consequently, increasingly higher loads are required for plastic deformation to continue.

When steel is deformed in a similar manner the metal behaves very differently. The steel appears to behave elastically in much the same manner, but a much greater load is required to initiate plastic deformation and when plastic deformation does occur, there is a lowering of the resistance to deformation and, consequently, the registered load is lower. This is shown by the solid line in Fig. 3. Our work has shown that substantial plastic deformation does not occur in a uniform manner as it does with aluminum, but occurs first at some point or points. This means that parts of the specimen reach the yield point and begin to deform plastically before other parts. The stress at which plastic deformation first occurs, is, according to general testing practice, taken to be the yield point of the steel as a whole.

It is the differences in thickness produced by plastic flow occurring at different points which give rise to the surface markings. As the alternate local slipping and work-strengthening continues, and the extent and number of the depressions in the surface of the metal increase, the condition is reached where the entire test piece has been so affected. The differences in cross sectional area then become relatively minute. In effect, this is a return to the original even surface. The total elongation occurring during this peculiar process has been conveniently referred to as the "yield point elongation." When all of the grains have slipped in this manner, the load-deformation curve begins to rise again as a relatively smooth curve. Since the yield point elongation is of the order of 10 pct or less, stretcher strains occur in stampings or those parts of stampings in which the elongation of the steel is of this amount. Mathematical equations, it seems to us, cannot be established for this portion of the load-deformation curve on the basis of homogeneous or heterogeneous plastic deformation because neither uniform nor nonuniform plastic deformation is occurring! How can either of these be taking place when there are large portions of the metal which are not plastically deforming at all?

It appears that for steel to behave like aluminum,

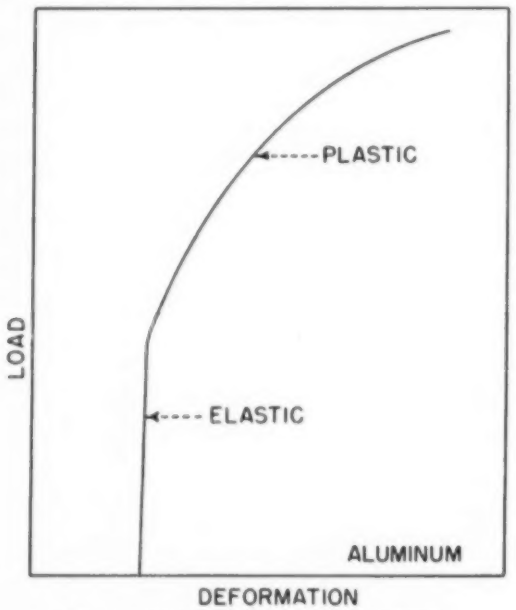


Fig. 2—Load-deformation curve of aluminum.

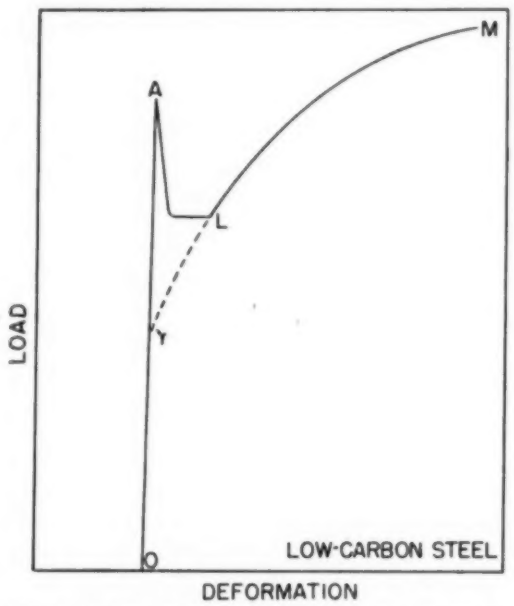


Fig. 3—Load-deformation curve of carbon steel containing free ferrite.

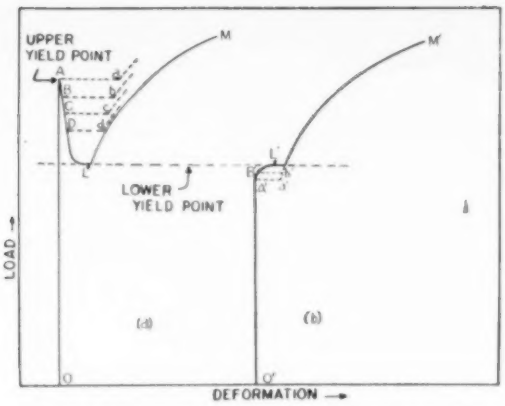


Fig. 4—Load-deformation curves of steels with and without upper yield points.

substantial plastic deformation should take place at the load Y in Fig. 3 and the load-deformation curve should be the curve *OYLM*. For some unexplained reason, however, the load Y is "overshot" and substantial plastic flow does not commence until the load *A* has been reached. This point has long been known as the "upper yield point." At the instant plastic deformation occurs, then, the steel finds itself overloaded, so to speak, with a resistance to further plastic deformation of only the load Y. The further behavior of the first increment of metal which has deformed plastically is dependent entirely upon its reaction to the precarious and unstable situation in which it finds itself. Because of the high load existing at the moment substantial plastic deformation occurs, the metal, because of its then lowered resistance to further plastic deformation, must deform at a very high speed, and it does so. The amount of metal forced to a great speed of deformation is partly governed by the amount of elasticity remaining in the other parts of the specimen and of the testing machine, and it is for these and other reasons that the downward path of the load-deformation curve veers away from the portion of the curve denoting elastic deformation. It should be emphasized that substantial plastic deformation may and often does occur at several isolated points instead of at just one point.

The following is a more detailed explanation of what we believe occurs: when the load *A*, Fig. 4a, is reached, the first increment of metal deforms plastically at the high load which it has built up for itself while in the elastic state. And, since it now has the resistance to further plastic deformation of only the load Y of Fig. 3, it does what it is forced to do, namely, travel at a high speed along the dotted line *A-a*. At the next instant, two other small increments, one on either side of the first, deform plastically at the load *B* an amount equal to *B-b*. The load on the specimen drops—first, because the metal has only the resistance to further plastic deformation of the load Y; second, because there is a concentration of stress at either end of the local constriction; third, there is now present some metal which has been cold-worked and this in itself throws a higher stress on the undeformed adjoining crystalline grains; and fourth, because the increment's speed of travel is greater than the head speed of the testing machine.

The total load registered by the specimen never drops to the load Y but only to the load *L*, known as the "lower" yield point, because a balance is reached between 1—the increase in resistance of the metal undergoing plastic deformation, i.e., work-strengthening; 2—the increase in resistance of the metal to further deformation because of the high rate of deformation; and 3—the presence of metal in other parts of the gage length which has only been elastically deformed, and which must first be stressed to a value corresponding to the upper yield point before plastic deformation can occur.

The extremely important point to emphasize is that at the instant plastic deformation is initiated, it is not necessary to have present the load which the metal has built up for itself while in the elastic state, in order for plastic deformation to continue.

It should be emphasized, also, that whether or not an upper yield point is obtained in the load-deformation diagram, a yield point elongation cannot exist unless the steel possesses an upper yield point; and, further, that each increment of the steel must be stressed to the value of the upper yield point before plastic deformation can occur. In short, we believe that the true stress at the load *A* in Fig. 4a is the same as the true stress at the load *B'* in Fig. 4b.

Fig. 5—Schematic drawing of the Budd-developed roller leveler.

In this connection it should be emphasized that the presence or the absence of an upper yield point depends to such a large extent upon the tensile specimen itself—that is, whether it is properly aligned in the testing machine, the presence of stress concentrations such as minute surface defects, etc.,—that often it cannot be obtained at all. As Dr. Mehl once so aptly said, "it would seem as though the load was increased so carefully (in especially prepared specimens) that the steel had hardly become aware of it,—much as the tax load may be increased on an unsuspecting body politic!"

It has long been known[1] that if the steel has been cold-worked a sufficient amount by cold rolling, or roller leveling, the load-deformation curve does take the shape of the curve *OYLM* in Fig. 3. In the deep drawing of sheet and strip steel we have, for many years, used a combination of cold rolling and roller leveling in a specially made roller leveler which we designed and built, Fig. 5. By this means we have prevented the irregular surface markings (stretcher strains) from occurring during the deep drawing operation, and we have found that after the yield point phenomena have been removed in this manner, the steel can be deep drawn more easily and at a faster rate of deformation. This is because if the rate of deformation is too rapid, and the yield point phenomena have not been removed, the steel may fracture where plastic deformation first occurs, that is, at the first stretcher strain.

In order to ascertain the influence of the rate of deformation on the load-deformation curve of low carbon steels, we performed a great many experiments some years ago.[10] Briefly, it was found that the lower yield point, the yield point elongation, and the ultimate tensile strength increased as the grain size was made smaller and as the rate of deformation was increased. Due to limitations in our testing apparatus and methods of recording available at that time, rates of deformation of only 4.44 in. per in. per min were obtainable. This rate is some-

Fig. 6—High speed testing apparatus.

what below the average speed of most deep drawing operations which is of the order of 45 in. per in. per min. Therefore, in order to study the effects of much higher rates of deformation, we developed a testing apparatus shown in Fig. 6 which deforms and records the deformation of the steel at much higher speeds.

It consists of a hydraulic pump and ram system proportioned to allow a wide range of head speeds up to 450 in. per min and loads up to 3000 lb. The loads are recorded by means of a balanced bridge weighing system operating on a 1000 cycle carrier which transmits its signal to an oscillograph. Deformation is recorded with a microformer operating from the same carrier wave and feeding into the same oscillograph. Both load and deformation systems have positive integral calibrations that are activated with each run.

In this paper we have extended our experiments not only to include the influence of much faster rates of deformation on the load-deformation curve, but also to determine the effect of increasing the carbon in the steel.

We chose for our experiments five sheet steels having carbon contents as follows: 0.06, 0.21, 0.34, 0.48, and 1.03 pct. The amount of the other elements was substantially the same in all of the steels.

The steels were all 0.035 in. in thickness and were carefully heat-treated to produce pearlite and ferrite,* that is, they were heated above the critical range and cooled in air. Micrographs were taken of each steel and these are shown in Figs. 7 to 11. Examination will show, as would be expected, that as the carbon is increased the amount of pearlite increases and the amount of free ferrite decreases.

* Professor Howe's definition of ferrite is pure iron, or rather carbonless iron. The word is now more commonly defined as a solid solution in which α iron is the solvent and which is characterized by a body-centered cubic crystal structure. In this paper the latter definition applies.

Tensile specimens were made from each sheet and machined to the dimensions established by the ASTM for Standard Rectangular Tension Tests with a 2 in. gage length (E8-46).

The specimens were deformed at the following rates: 0.002, 0.018, 0.166, 1.500, 20.000, and 200.000 in. per in. per min.

It will be noted that the highest rate is some five times the average speed used in ordinary deep drawing operations and that these testing speeds represent a range of 100,000 to 1.

A series of load-deformation curves were made, Figs. 12 to 17, of the steels at different rates of deformation. The experimental data obtained from these curves were analyzed and are summarized in Table I and Figs. 18 to 22.

It may be seen in Fig. 18 that for any given steel the upper yield point increases as the rate of deformation increases. It may also be observed that the increase in the upper yield point for a given increase in the rate of deformation is independent of the

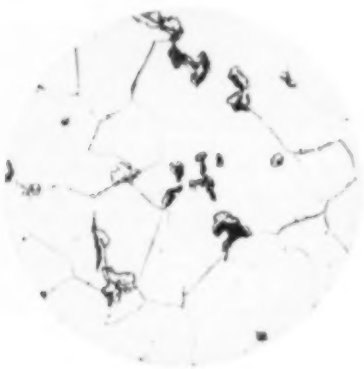


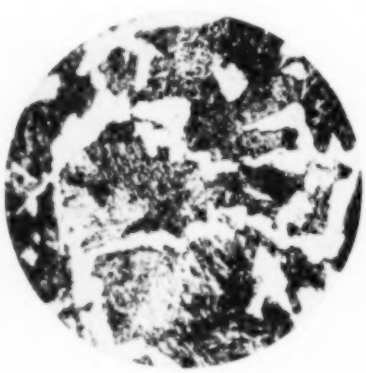
Fig. 7 (left)—Micrograph of 0.06 pct C steel. X500.

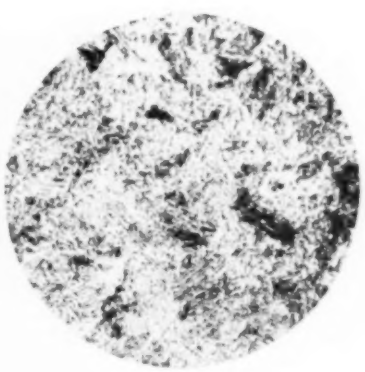
Fig. 8 (right)—Micrograph of 0.21 pct C steel. X500.

Fig. 9 (lower left)—Micrograph of 0.34 pct C steel. X500.

Fig. 10 (lower center)—Micrograph of 0.48 pct C steel. X500.

Fig. 11 (lower right)—Micrograph of 1.03 pct C steel. X500.





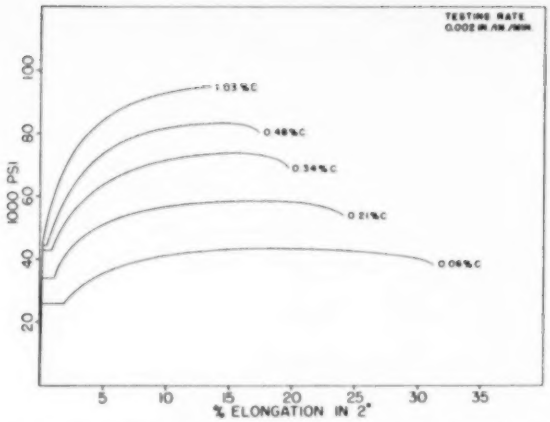


Fig. 12—Load-deformation curves of steels deformed at 0.002 in. per in. per min.

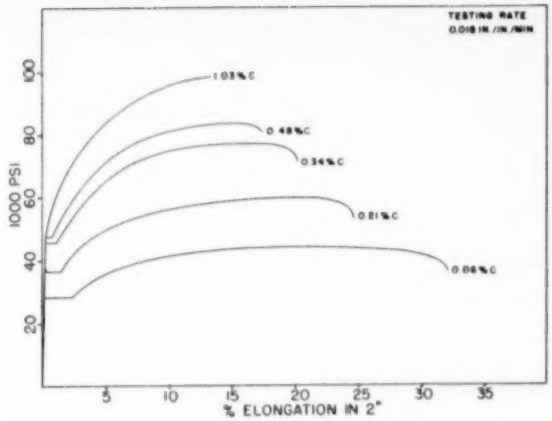


Fig. 13—Load-deformation curves of steels deformed at 0.018 in. per in. per min.

carbon content. However, when the carbon content is increased above the amount necessary to form the eutectoid, no upper yield point occurs, and, consequently, no lower yield point can exist. The apparently anomalous behavior of the hypereutectoid steel is not so much out of order, as it would seem, because we believe that all the upper and lower yield point phenomena are properties of free ferrite. For this reason, we have not included the curves of the "normally behaving" (if this term is permissible) hypereutectoid steels in Figs. 18, 19, and 20 which summarize the results of our experiments on the yield point phenomena of the hypoeutectoid steels containing free ferrite.

In this connection, some experiments were made with the hypereutectoid steel heat-treated so as to cause the carbon to be in the spheroidized condition, thus producing free ferrite. In these experiments we found that an upper and a lower yield point occurred at all rates of deformation.

In other words, when free ferrite is made to disappear by heat treatment, or when it is prestressed by cold working, or when it is cooled rapidly from just below the critical range, or when it is treated by heating in wet hydrogen,[7] the upper yield point

Table I. Experimental Data Giving Tensile Properties of Steels of Different Carbon Content Deformed at Different Rates of Deformation

Speed of Test, In. per In. per Min	Pct Carbon	Upper Yield Point	Lower Yield Point	Yield Point Elongation	Elongation, Pct in 2 In.	Ultimate Tensile Strength
0.002	0.06	25,000	26,000	1.75	31.50	43,500
0.018	0.06	28,000	28,000	2.50	32.25	44,000
0.166	0.06	31,000	29,500	3.00	33.25	45,000
1.500	0.06	34,000	31,500	4.00	34.50	46,500
20.000	0.06	37,500	33,500	5.25	36.50	46,500
200.000	0.06	40,500	35,500	6.75	39.00	47,500
0.002	0.21	33,000	34,000	1.25	24.25	59,000
0.018	0.21	36,500	36,000	1.50	24.75	60,000
0.166	0.21	40,000	38,000	2.00	25.50	61,000
1.500	0.21	43,000	41,000	2.50	26.00	62,500
20.000	0.21	47,000	44,000	4.50	26.75	63,500
200.000	0.21	51,000	46,500	4.75	27.25	65,000
0.002	0.34	38,500	43,000	1.00	20.00	74,000
0.018	0.34	41,500	45,000	1.10	20.25	77,000
0.166	0.34	45,000	48,000	1.25	20.50	80,500
1.500	0.34	48,500	50,500	1.75	20.75	82,000
20.000	0.34	52,000	53,500	2.25	21.00	86,000
200.000	0.34	56,000	56,000	3.25	21.25	88,500
0.002	0.48	44,000	44,500	0.50	17.5	83,500
0.018	0.48	47,500	47,000	0.60	17.5	86,500
0.166	0.48	50,500	50,000	0.75	17.5	89,000
1.500	0.48	53,500	53,000	1.00	17.5	91,500
20.000	0.48	57,000	56,000	1.25	17.5	94,500
200.000	0.48	60,500	59,500	1.50	17.5	97,000
0.002	1.03		45,500*		13.5	95,000
0.018	1.03		39,500*		13.5	98,000
0.166	1.03		45,000*		13.5	101,000
1.500	1.03		52,000*		13.5	104,000
20.000	1.03		60,000*		13.5	109,500
200.000	1.03		58,500*		13.5	114,500

* Yield strength—not lower yield point—that is, 0.5 pct extension under load.

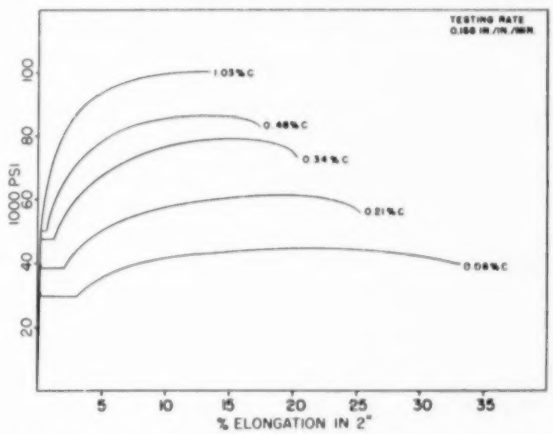


Fig. 14—Load-deformation curves of steels deformed at 0.166 in. per in. per min.

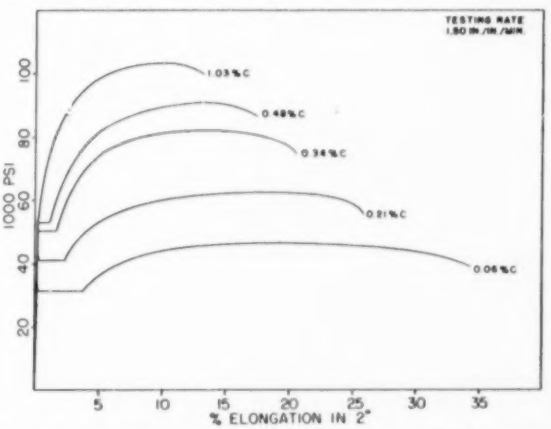


Fig. 15—Load-deformation curves of steels deformed at 1.50 in. per in. per min.

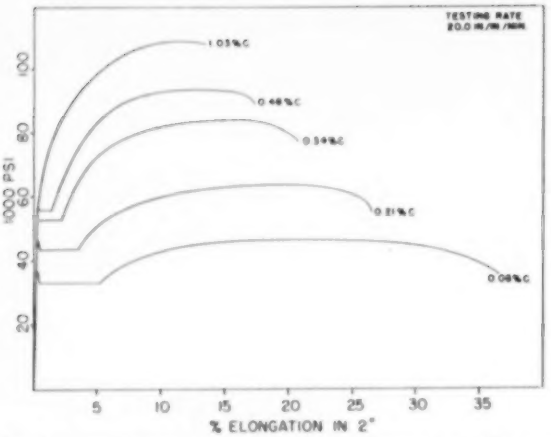


Fig. 16—Load-deformation curves of steels deformed at 20.00 in. per in. per min.

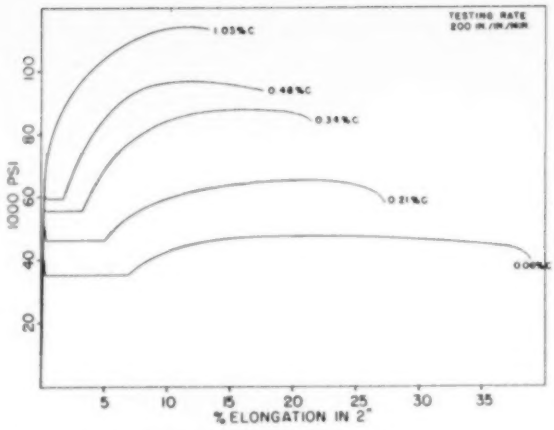


Fig. 17—Load-deformation curves of steels deformed at 200.00 in. per in. per min.

disappears from the load-deformation curve, and, consequently, the lower yield point disappears too.

As may be seen from the curves shown in Fig. 19, the lower yield point increases as the rate of deformation is increased and as the carbon is raised. And it may also be seen that as the carbon is raised, the lower yield point becomes more affected by an increase in the rate of deformation.

The lower yield point gives, we believe, a much more reliable indication of the end of substantial elastic behavior of the steel than the upper yield point because it is much less affected by those variables of testing which are difficult to control, as we have already mentioned.

It is of particular importance to note that the yield strength (0.5 pct extension under load) of the hypereutectoid steel containing no free ferrite is lower even at very high rates of deformation than some of the steels containing very much less carbon. In other words, the hypereutectoid steel, unencumbered by the yield point phenomena, deforms in much the same manner as does cold-worked low carbon steel, that is, the load-deformation curve is smooth from origin to fracture.

The amount of yield point elongation, Fig. 20, increases as the rate of deformation increases and decreases as the amount of carbon is raised. The amount of yield point elongation is less affected by an increase in the rate of deformation as the carbon is raised.

The total elongation, Fig. 21, either increases or does not change as the rate of deformation is increased, and decreases as the amount of carbon in the steel is increased. The amount of total elongation is less affected by an increase in the rate of deformation as the carbon is raised.

The ultimate tensile strength, Fig. 22, increases as the rate of deformation is increased, and increases as the carbon in the steel is increased. The ultimate tensile strength is more affected by an increase in the rate of deformation in the higher carbon steels than it is with the lower carbon steels. From the converging of the curves for the low carbon steels shown in Fig. 22, the very interesting and significant observation can be made that the ultimate strength of absolutely pure iron would be very little affected by high rates of deformation.

In summarizing the data, we can make the following statements regarding plain carbon steel:

1—All the load-sustaining properties increase

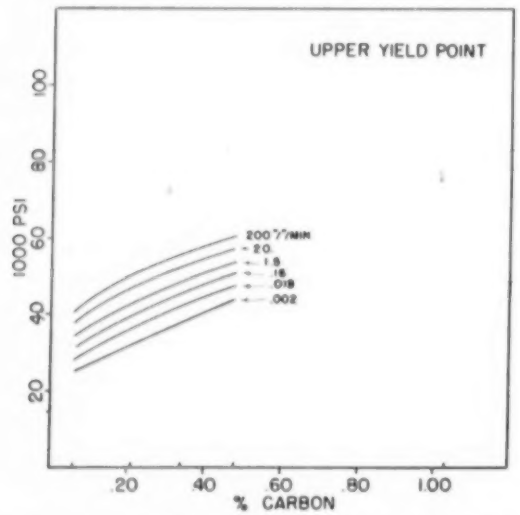


Fig. 18—Curves giving a summary of data of upper yield points of steels at different rates of deformation.

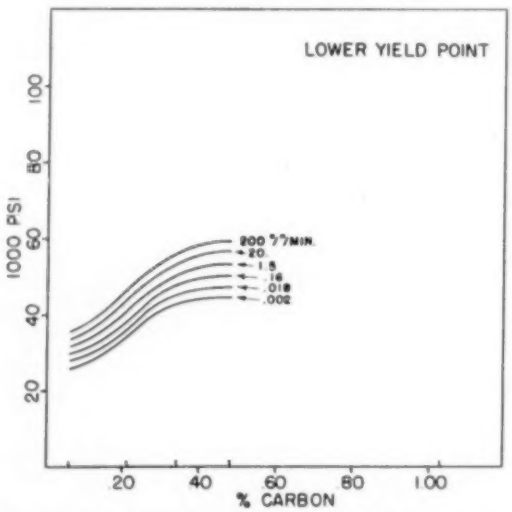


Fig. 19—Curves giving a summary of data of the lower yield points of steels at different rates of deformation.

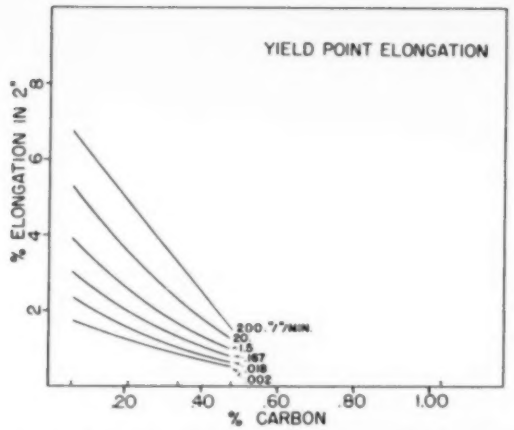


Fig. 20—Curves giving a summary of data of the yield point elongations of steels at different rates of deformation.

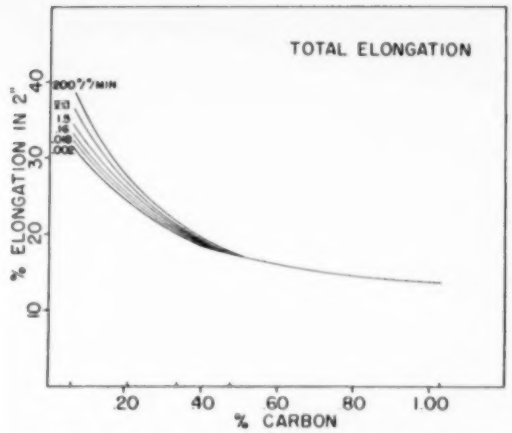


Fig. 21—Curves giving a summary of data of the total elongations of steels at different rates of deformation.

with increasing rates of deformation.

2—All percentage elongations either remain constant or increase with increasing rates of deformation.

3—All load-sustaining properties increase as the amount of free ferrite is decreased.

4—All percentage elongations decrease as the amount of free ferrite is decreased.

From a practical standpoint, these experiments, together with others which we have made, indicate that the plasic behavior of steel imposes no limitations on new methods of deep drawing involving much higher rates of deformation.

I should like to acknowledge to my colleagues, Dr. Ralph Leiter, Mr. Herbert Van Sciver, and Mr. Paul Nelson, my appreciation for their valuable assistance in the preparation of this paper. I should like, also, to express to Mr. Edward G. Budd, Jr. my gratitude for his interest and encouragement.

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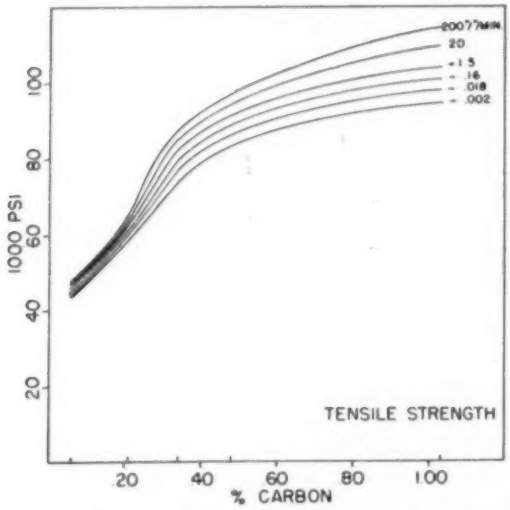

Fig. 22—Curves giving a summary of data of the tensile strengths of steels at different rates of deformation.

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Vapor Pressure of Zinc In the Reduction of ZnS by Cu and Fe

by A. W. Bethune and L. M. Pidgeon

The equilibrium vapor pressure of zinc has been determined over the systems:

$$ZnS(s) + Fe(s) = FeS(s) + Zn\ (vapor)$$

and

$$ZnS(s) + 2Cu(s) = Cu_2S(s) + Zn\ (vapor)$$

by reacting the components in an evacuated tube containing a thin copper fiber, and allowing equilibrium to be established with respect to the brass formed and the zinc in the vapor phase. The composition of the brass formed was determined and equilibrium vapor pressure values obtained from existing data. Between 850° and 1000°C, values for the first reaction ranged from 8 to 58 mm Hg; for the second reaction from 1.8 to 22 mm Hg.

THE direct reduction of metallic sulphides may be indicated by an equation of the form

$$MS + X = XS + M \qquad [1]$$

where X is some suitable reducing agent.

In the case where M is a metal of relatively high volatility, the use of vacuum will displace the equilibrium to the right at comparatively low temperatures in the face of the usually unfavorable thermochemistry. For this technique to be feasible, MS, X, and XS, must of course be nonvolatile compared to M. In this regard, zinc becomes an obvious metal both from the point of view of its volatility and the fact that most commercial ore deposits of this metal occur as the sulphide, and its direct reduction would avoid the expensive roasting process necessary prior to present day reduction methods.

Two reducing agents are of interest, namely copper and iron, with the former having the added attraction of being relatively easily regenerated by oxidation in the copper converter.

The possibility of these reactions has been considered before. Imbert[1] patented a process whereby zinc sulphide was reduced by either copper or iron. The process as described took place at atmospheric pressure and, at the high temperatures required, the system was molten, resulting in the formation of a matte with the consequent reduction in the activities of the reactants.

Peterson[2] did further experimental work on these reactions and, although promising results were obtained on a small scale, attempts to increase the size of the furnace led to excessive "blue powder" formation.

The early workers failed to realize the large reduction in temperature afforded by the use of vacuum and its desirable results.

More recently, the direct reduction of zinc sulphide by iron has been the subject of a thermodynamic investigation by Kelley,[3] and Gross and Warrington[4] have studied the kinetics of the reaction in the temperature range 900° to 1000°C, their experiments being conducted using vacuum and indicating that the reaction would proceed practically to completion in 1 to 3 hr, depending on the temperature.

A qualitative examination of the system ZnS-Cu carried out at this University indicated that 98 pct of the theoretical zinc in the charge could be recovered in 1 hr at 1000°C when operating under reduced pressure.

The purpose of this research program was to study the equilibrium of the two reactions. During the investigation, reference to the experimental work of Schenk[5] was found but, due to lack of detail in the report, it was felt that it would be desirable to continue the equilibrium measurements.

Selection of Method

The measurement of vapor pressure of metals presents obvious problems resulting from the high temperatures which must be employed. In the present case, the production of the "reaction pressure" introduces a further difficulty since a chemical reaction must proceed before any metal vapor pressure is produced, resulting in depletion of the re-

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actants. This reaction must proceed and approach an equilibrium pressure at which further reaction ceases. Experiments used first the entrainment method, as described by Pidgeon and King,[3] and it was found that reaction rates were very slow near the equilibrium pressure, although experiments in vacuo had given rapid rates.

The advantages of a static method are obvious, and it was decided to measure the pressure of zinc by allowing the zinc vapor to come to equilibrium with copper and analyze the brass so produced. The vapor pressure of zinc over brasses has been measured by several workers and satisfactory results are available. As every brass of a particular composition has an equilibrium vapor pressure of zinc associated with it at each temperature, then the converse must hold true; that is, at equilibrium, a vapor pressure of zinc must create an equilibrium state with any copper with which it is in contact. The problem is, therefore, to achieve this equilibrium state.

Hargreaves[4] modified a technique described by Euken[5] to obtain the vapor pressures of zinc above brasses in which the brass sample was held at an elevated temperature in an evacuated tube until equilibrium had been achieved and then the section of the tube remote from the brass sample cooled until condensation occurred from which the vapor pressure of zinc in the system was determined.

Experimental

Materials: Zinc sulphide used in the experimental work was in the form of clear amber sphalerite. Chemical analysis of this material indicated 66.5 pct Zn. Spectroscopic analysis showed the presence of trace quantities of copper, iron, sodium, and cadmium. This material was ground to pass a 200 mesh screen.

Chemically precipitated copper analyzing 99.9 pct Cu and passing 200 mesh was used as the reducing agent in studying the ZnS-Cu system, and was heated in a stream of hydrogen prior to each experiment to prevent any possibility of oxide contamination. The iron used in the subsequent experiments was also of reagent grade, total impurities being 0.02 pct. A fine electrolytic copper fiber, 3 mm wide and 0.04 mm thick, was used as a "gettering" agent for the zinc vapor.

Procedure: Reduction of Zinc Sulphide by Copper: A charge of 6 g was mixed in stoichiometric proportions and placed in one end of a transparent quartz reaction vessel, 10 mm ID and 10 cm long. This weight of charge was sufficient to produce 1.5 g of zinc. A copper fiber, carefully polished to remove oxide and grease coatings and accurately weighed, was inserted in the other end, the tube evacuated to a residual pressure of 5 microns and sealed off under vacuum. The system was placed in the furnace which was then sealed. The temperature was controlled to ±2°C. Thermocouples were calibrated against a standardized Pt-Pt-Rh couple.

Curves were obtained from Herbenar's[6] values for the vapor pressure of zinc above brasses at various temperatures. Isothermals were taken through these curves at appropriate temperatures yielding a plot of vapor pressure vs composition. These values were used in determining the pressure of zinc vapor within the system after analyzing the brass produced.

To obtain the time required to reach equilibrium, reaction vessels were left at temperature for periods

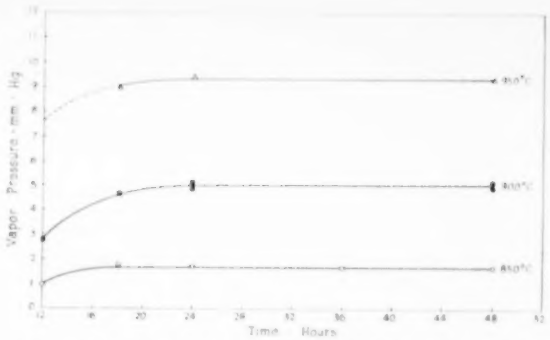

Fig. 1—Reaction pressure above the system ZnS + 2Cu at 850°, 900°, and 950°C vs time at temperature.

of 12, 18, 24, and 48 hr. At the end of these four times, the tube would be removed and quickly cooled.

Three independent checks were obtained on the composition of the brass produced: 1—increase in weight over the copper fiber originally used, 2—electrolytic analysis of the brass for copper, and 3—gravimetric determination of the zinc by precipitation with di-ammonium hydrogen phosphate. All these methods agreed within 0.2 pct. This error corresponds to a maximum variation in zinc pressure of 0.5 mm. Although no analysis of sulphur was carried out, the deposit formed possessed a bright mirror finish and it is felt that the degree of contamination was negligible.

Fig. 1 shows in graphical form the results obtained for three temperatures. The graph shows that a constant condition is achieved in all cases by 24 hr. In spite of this, all subsequent experiments were maintained at temperatures for 48 hr as an additional safety factor.

Since the reaction mixture was depleted with respect to zinc as the brass was formed, a large excess of charge was essential. The initial experiments in this series were performed using 0.8 to 1.0 g of copper. These were conducted at 900°C and, on comparing with the values obtained using 0.2 g weights showed an apparently lower reaction pressure, although the weights of zinc absorbed were greater by a factor of three. Consequently, further experiments were conducted with decreasing weights of fiber. The results are plotted in Fig. 2. These experiments showed that constant composition was attained in this system using weights of

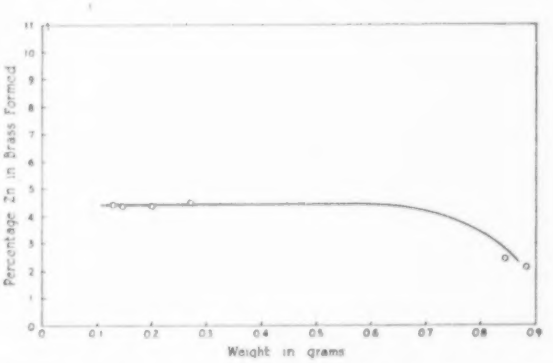

Fig. 2—Reduction of ZnS by copper. Effect of decreasing the weight of copper foil. Experiments, 24 hr at 900°C.

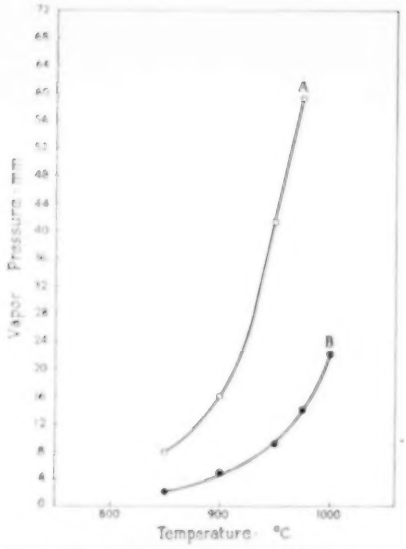

Fig. 3—Vapor pressure vs temperature for the systems.
Curve A (reaction 1)—$ZnS(s) + Fe(s) = FeS(s) + Zn(vapor)$.
Curve B (reaction 2)—$ZnS(s) + 2Cu(s) = Cu_2S(s) + Zn(vapor)$.

copper less than 0.3. The results shown in Fig. 3 were obtained using weights of copper fiber of 0.1 to 0.2 g.

Reduction of Zinc Sulphide by Iron: This reaction was studied using the technique already described. Stoichiometric charges of the material were heated in the evacuated tubes for 48 hr, and the copper fiber analyzed as before. The reaction pressures determined are shown in Fig. 3, curve *A*.

Alternate Method

The above results, obtained by an indirect method which depends upon the work of others, are also dependent on the attainment of equilibrium both over the reaction mixture and the brass. Corroborative results were obtained using the conventional entrainment method.[9]

In this method, a current of inert gas is passed through the sample until saturation is achieved. The metal vapors are condensed and weighed, and the volume of the inert gas also measured. From the known volume of the inert gas and the calculated volume of the metal, the partial pressure of the metal vapor may be obtained by application of the gas laws.

The ideal conditions inherent to accuracy are: 1—It is essential that complete saturation of the inert carrier gas must be established and the reactants must not be appreciably depleted. 2—Temperature, pressure, and rate of flow of the carrier gas must be constant and accurately measured. 3—Condensation of the zinc must be complete and the amount accurately determined. 4—The reacting charge should in effect be heated instantly to the reaction temperature and cooled instantly at the end of the measured period.

When these conditions had been met, results of the vapor pressure over ZnS-Cu were obtained agreeing within 5 pct with the values obtained using the previous method. The entrainment method, although apparently very simple, did not give consistent results at first. It was difficult to achieve saturation of the gas stream. The method was tedious and cumbersome compared with that described above. Table I gives a comparison of the methods.

Vapor Pressure of Zinc Over System Marmatite-Iron

Most commercial zinc ores contain varying percentages of iron associated in some manner with the zinc sulphide. These ores are termed marmatites and are usually designated by the formula (Zn,Fe)S. Little information is available on the actual method of association. An X-ray examination of marmatites containing varying percentages of iron[10] showed a continuous increase in the lattice parameter which, in view of the similarity in the ionic radius of zinc and iron would suggest a substitutional solid solution. If this solid solution had any appreciable free energy of formation, this should be detectable by a decrease in the activity of the zinc sulphide with a consequent decrease in the vapor pressure of zinc over the system:

$$(Zn,Fe)S + Fe = Zn + FeS \qquad [2]$$

when compared with the ZnS-Fe system.

The above reaction was studied over the temperature range (850° to 1000°C) using marmatites of 7.6 and 8.6 pct Fe.

An insignificant decrease was noted at the lower temperatures. At 950°C, however, the reaction using marmatite containing 8.6 pct Fe indicated a reaction pressure 2.2 mm less than when pure sphalerite was used. This decrease was, however, of too low a magnitude to deduce any quantitative conclusions, although it does suggest a very low free energy of solution.

Discussion of Results

The equilibrium constants associated with reactions 2 and 1 are given by:

$$K_2 = \frac{p_{Zn} \cdot a_{Cu_2S}}{a_{ZnS} \cdot (a_{Cu})^2} \qquad [3]$$

and

$$K_1 = \frac{p_{Zn} \cdot a_{FeS}}{a_{ZnS} \cdot a_{Fe}} \qquad [4]$$

When it is possible to assign unit activity ($a = 1$) to the other reactants in the system, then the equilibrium constant may be identified with the partial pressure of zinc.

An examination of the Cu-S and Fe-S phase diagrams shows that, at the temperatures involved, all the reactants and products, with the exception of zinc, should remain solid and that the stable sulphides at these temperatures are Cu_2S and FeS with no solid solubility of copper or iron in their respective sulphides.

An X-ray examination of the products of the ZnS-Fe system showed no detectable distortion of the zinc sulphide lattice after 48 hr at 900°C. A comparison of the ionic radii (Zn = 0.74A, Fe = 0.75A, Cu = 0.96A) would indicate that iron would have a greater tendency to form a solid solution with zinc sulphide than would copper, and since no indication of solid solution was found in this case it is reasonable to assume that no solid solution should occur in the ZnS-Cu system. For these reasons, unit activities may be ascribed to zinc sulphide, copper sulphide, and iron sulphide.

In reaction 2 errors will be introduced in any thermodynamic calculation in which unit activity is assigned to copper. The Cu-Zn phase diagram shows

a solid solubility of zinc in copper up to 38 pct by weight. Although deviations in the activity of the copper should not vary too greatly from ideality in this region, the fact that in Eq. 3 its activity becomes a squared function makes its consideration necessary.

Birchenall and Mehl[11] using the Gibbs-Duhem equation have calculated the activities of copper in brasses from the experimental results of Hargreaves,[6] Herbenar et al,[8] and Schneider and Schmid.[12]

In the case of iron, the limited solid solubility of zinc in iron at the temperatures concerned suggests that no appreciable decrease in the activity of the iron should be expected.

Assuming that ΔH, the calorimetric heat of reaction, does not vary appreciably over the temperature range involved, the integrated form of the Van't Hoff equation becomes

$$\ln K = \frac{-\Delta H}{RT} \qquad [5]$$

and, if $\ln K$ is plotted against $1/T$ the result should be a straight line of slope $-\Delta H/R$. In the case of the ZnS-Fe system, the direct measurement of the slope should yield the true value of $-\Delta H/R$. In this case, the line corresponded to a calorimetric heat of reaction of + 45,130 cal.

However, in the case of the ZnS-Cu system, the equilibrium to be considered is not between zinc sulphide and copper but between zinc sulphide and a brass of some composition related to the pressure existing over the system. It is impossible to determine this composition precisely. It appears reasonable to assume that the composition of the brass in equilibrium with unreacted zinc sulphide will be the same as the composition determined for the foil. With this assumption, the reduced activity of the copper may be determined and a calorimetric heat of 49,800 cal is calculated.

Summary

The vapor pressure of zinc over the reactions:

$$ZnS + Fe = FeS + Zn \quad [Reaction\ 1]$$

$$ZnS + 2Cu = Cu_2S + Zn \quad [Reaction\ 2]$$

was determined experimentally. In reaction 1 (curve A, Fig. 3) it was found to vary from 1.8 to 22 mm Hg from 850° to 1000°C. In reaction 2 (curve B, Fig. 3) the pressure varied from 7.6 to 58.2 mm Hg over the temperature range 850° to 975°C.

Calculations based on these measurements indicated the calorimetric heat of reaction at a mean temperature of 1200°K to be:

Table I—Comparison of Alloy Formation and Entrainment Methods

Method	Temperature, °C	Vapor Pressure, Mm
Alloy formation	850	1.8
Entrainment	850	1.8
Alloy formation	900	5.2
Entrainment	900	4.9

Reaction 1

$$\Delta H = +49{,}800 \text{ cal}$$

Reaction 2

$$\Delta H = +45{,}100 \text{ cal}$$

Values of the heat of reaction calculated from existing data and from the experimental data determined in this investigation are listed as follows:

For the ZnS-Cu system	
H_{1200} (calculated from existing data)	+54,100 cal
H_{1200} (from this investigation)	+49,800 cal
Difference	+4,300 cal
For the ZnS-Fe system	
H_{1200} (calculated from existing data)	+48,400 cal
H_{1200} (from this investigation)	+45,100 cal
Difference	+3,300 cal

These differences agree within the degree of experimental error.

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Technical Note

Kinetics of Galvanizing

by D. J. Blickwede

WHEN iron is dipped in molten zinc at temperatures in the range 840° to 930°F, the two metals react to form layers of Fe-Zn compounds which adhere to the iron. At the galvanizing temperature, the successive layers are:[1] γ (Fe_3Zn_{21}), δ_1 (FeZn$_7$), and ζ ($FeZn_{13}$), in conformity with the Fe-Zn constitution diagram.

There is no quantitative information in the literature on the rates of growth of the individual alloy layers over the temperature range 840° to 930°F. Rather all the past experiments have studied the loss in weight of iron as a function of galvanizing

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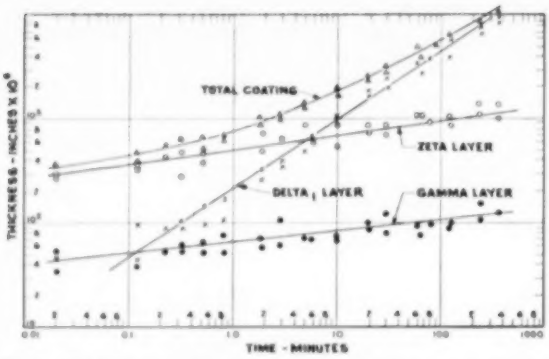

Fig. 1—Thickness of alloy layers after immersion in pure zinc at 840°F for various periods of time.

time and temperature. Generally, it has been found[2] that the weight loss-time curve is parabolic in form at 840°F, but with increasing temperature it begins to assume a more linear form until at 930°F it is a straight line. Above 930°F the curve again becomes parabolic. The rate of iron loss is also most rapid at 930°F, being less at temperatures below and above this point.

These and other published data have led to the commonly accepted assumption that the rate determining process of the galvanizing reaction at temperatures up to 900°F is diffusion of iron from the base metal and zinc from the spelter through the coating, where they form ζ and γ at the ζ-Zn and Fe-γ interfaces, respectively. However, this postulate has never been checked by actual thickness measurements of the alloy layers.

To obtain such information, suitably cleaned, pickled and fluxed specimens, 1½ in. square by 22 gage, of a 0.08 pct C sheet steel were dipped in pure zinc for various periods of time at 840°, 870°, and 900°F. Transverse sections of the specimens were polished and etched using the techniques developed by Rowland.[1] The thickness of each alloy layer was measured with a microscope, and all values are the average of at least ten readings on a specimen. Typical of the results are the data for 840°F plotted on logarithmic coordinates in Fig. 1. The data at this temperature and at 870° and 900°F form straight lines on these coordinates, and hence may be described by an empirical equation of the form

$$y = kt^n \qquad [1]$$

where y is the thickness in inches of the particular alloy layer at t minutes, and k and n are constants. Numerical values of the constants for each alloy layer at each temperature were evaluated by the method of least squares and are listed in Table I.

Table I. Values of Constants for Each Alloy Layer

Temperature, °F	γ Layer		δ_1 Layer		ζ Layer	
	k	n	k	n	k	n
840	8.29×10^{-5}	0.090	2.63×10^{-4}	0.60	5.37×10^{-4}	0.156
870	5.93×10^{-5}	0.109	3.11×10^{-4}	0.63	6.31×10^{-4}	0.28
900	1.39×10^{-5}	0.216	3.26×10^{-3}	0.64	y not measurable	

It may be shown that if the growth of the coating is solely controlled by diffusion of zinc and iron through the thickening layers, the constant n in Eq. 1 would be 0.50. In no case did the measured values of n approach this value. Hence, it appears that diffusion is not the rate determining process in galvanizing.

This conclusion is further substantiated by consideration of the temperature dependence of the constant, k, in Eq. 1. If diffusion were the rate determining process,

$$k = Ke^{-Q/RT} \qquad [2]$$

where Q is the activation energy of the process, R the gas constant, and T the absolute temperature, and a graph of log k vs $1/T$ would be a straight line. As shown in Fig. 2, this is not the case for the present data.

It was mentioned that some of the literature indicates the weight-loss vs time curves give values of n in Eq. 1 of 0.5. However, the growth of the total coating ($\gamma + \delta_1 + \zeta$) for the present data, which might approximate the iron loss behavior, does not verify this, see Fig. 1. In fact, the empirical equation describing the growth of the total alloy coating must be quite complex, since it does not form a straight line on logarithmic coordinates.

The present data do not bring out any mechanism to account for the fact that the rate of growth of the alloy layers during galvanizing is not controlled by diffusion. It is probable that sloughing of the ζ layer into the zinc bath causes the slow apparent rate of growth of this layer. Also such features as slowness of the reactions at the alloy phase boundaries or cracks in the individual layers may be involved in the mechanism of growth.

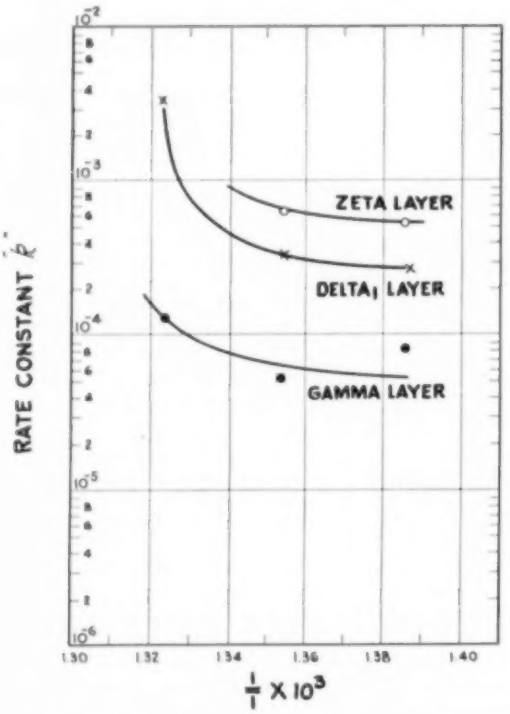

Fig. 2—Rate constant k in equation $y = kt^n$ vs the reciprocal of the absolute temperature.

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Recrystallization and Stored Energy

by H. P. Leighly, H. L. Walker, and J. W. Marx

A relationship between recrystallized grain size and prior deformation is predicted from elementary statistical considerations, and reasonable agreement with experiment is obtained.

RECRYSTALLIZATION phenomena have received much theoretical and experimental attention, and very adequate discussions of the various mechanisms suggested have been given by Anderson and Mehl,[1] Cook and Richards,[2] and Burgers,[3] and others. It suffices to note here that the initial concepts fitted one of two general hypotheses: 1—The new crystals are nucleated within microscopic regions at which there is a concentration of internal stress, i.e., volume elements of maximum strain energy. 2—The new crystals have their inception in volume elements of minimum strain energy.

In a comprehensive early review of the subject, van Arkel[4] considered both possibilities and came to the conclusion that hypothesis 2 was inconsistent with the experimental fact that the number of nucleations increased with increasing deformation. He suggested that, if allowance was made for a preliminary atomic rearrangement at the points of large internal strain, hypothesis 1 provided the more reasonable concept.

Following the initial observations of Collins and Mathewson[5] and Crussard,[6] the systematic X-ray investigations of Cahn[7] and Guinier and Tennevin[8] established the existence of a polygonized structure in metals that had been cold-worked, and subsequently annealed, under conditions such that recrystallization did not occur. This new experimental evidence by no means disproved the first nucleation hypothesis, a fact recognized by both Beck[9] and Cahn,[10] who independently suggested nucleation mechanisms based on the idea that regions of large strain might polygonize before the bulk of the less deformed material. These mechanisms, together with others recently proposed,[3] are dependent upon the prior existence of some degree of polygonization in the deformed material.

On the other hand, a critical examination of the published data leads to the supposition that polygonization may not be the necessary precursor of recrystallization, but merely its favored energetic competitor. In regions where the lattice distortion is not too severe, the limited adjustment afforded by polygonization may permit the lattice to drop to a relatively stable low energy state in which the nucleation of a new crystal becomes improbable, even at elevated temperatures. Such structures, of course, might provide a fertile field for the growth of nuclei, if these could be introduced. In regions of concentrated lattice distortion, polygonization alone may not be able to accomplish an adequate strain reduction, and in these volume elements sufficient thermal activity permits the more drastic atomic rearrangement involved in nucleation.

Completely polygonized structures are known to withstand extended heating close to their melting points,[11] with no other effect than a slow enlargement of some of the subgrains at the expense of others. Once started, macroscopic recrystallization might be expected to go to completion in a matter of minutes under similar heat treatment. Crussard[12] and his coworkers have found that recrystallization may occur in single crystals of impure (about 99.7 pct) aluminum without any detectable prior polygonization. The indication here is that large Cottrell impurity atmospheres inhibit dislocation movement, thus suppressing polygonization to such an extent that the alternative process, recrystallization, dominates the lattice restoration.

Experimental studies relating recrystallization directly to stored energy have not, at the present time,

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been carried out on a comprehensive basis. The most extensive of the earlier measurements of stored energy have been summarized in a series of papers by Taylor and his associates.[13-15] The ability of polycrystalline copper to store energy, for example, was found to approach saturation for reductions of more than 0.7 in compression. Below that deformation the ratio of stored energy to work energy expended was of the order of 10 pct. Both this work and the more recent initial results reported by Crussard[12] indicate that a portion of the stored energy is released in recovery processes prior to recrystallization, while the greater part of the balance is recovered early in the recrystallization itself.

No discussion of stored energy experiments would be complete without some mention of the remarkable results reported by Suzuki.[16] The extraordinary feature of this work was the report that, after compressional reductions of polycrystalline copper ranging from about 0.05 to about 0.60, followed by heating at a rate of 2°C per min from room temperature to above 300°C, virtually all of the stored energy was recovered, yet recrystallization was noted in only one specimen.

In view of the fact that many investigators, among them Crussard,[12] find recrystallization proceeding with appreciable velocity below 200°C in cold-worked copper, the present writers attempted to verify Suzuki's work in this respect. Single crystals of spectrographically pure (99.999 pct) copper were deformed in compression and heated at 2°C per min. Some bending and "barreling" of the specimens occurred, but the deformation may still be presumed to be relatively homogeneous compared to that in a grain of polycrystalline material compressed by the same amount. In every case in which the compressional reduction exceeded 0.1, microscopic new crystals were formed on heating to 330°C, while for larger reductions, of the order of 0.5, a part of the recrystallized grains were macroscopic in size by the time the temperature reached 290°C, the lowest temperature at which any specimens were removed for observation.

Thus nucleation in single crystals may be said to occur below 300°C at the given heating rate. Presumably the process would be well advanced at even lower temperatures in polycrystals. In view of this observation, the second stage of energy release, which Suzuki observed above 200°C, may possibly be regarded as that associated at least with the nucleation, if not the extended growth, of new crystals. The fraction of recrystallized volume may easily have been too small to significantly lower the hardness, or be unambiguously distinguished from the rest of the polycrystalline matrix.

The first stage of energy release, which attained its maximum velocity between 150° and 200°C in Suzuki's experiments, may include some contributions from the coalescence of impurity atoms and edge-type dislocations. The number of available dislocation sites would, of course, depend upon the cold-working. Suzuki's copper contained more than 10^{19} impurity atoms per cubic centimeter, all of which could be accommodated for a reasonable cold-worked dislocation density of 10^{12} cm per cu cm. Assuming a binding energy of 0.5 electron volt,[17] in the limiting case in which all the impurities were condensed along dislocation lines, the exothermic reaction could produce between 0.1 and 0.2 cal per g, which is of the same order of magnitude as the observed effect. This very rough estimate, of course, merely indicates that the impurity contribution should be carefully considered in calorimetric studies of stored energy.

On the basis of the hypothesis that nucleation occurs in volume elements of maximum strain energy, the postulates of elementary statistical mechanics may be applied to the problem of recrystallization after deformation. The task is one of predicting the number of successful nucleations, or new grains, that result when an annealed metallic solid is cold-worked and subsequently heated at a constant temperature for a time just sufficient to convert the deformed matrix essentially into new grains. The required idealizations are that the number of nucleations be large, and that the deformation be macroscopically homogeneous.

A first approach to the problem may be made by considering a quantity of stored energy W as distributed throughout n microscopic volume cells comprising one unit volume of material, subject to the condition that a lattice disorganization corresponding to a cell energy level Q is necessary before nucleation can occur in that cell. Even though some fraction of this energy may be recovered by other processes prior to recrystallization, the residual stored energy W' and the residual nucleation energy Q' may be presumed to be proportional to W and Q, and the initial distribution would then not be materially altered. The mean energy per cell is then simply W/n, which may be treated as a potential distribution modulus analogous to the well-known thermal distribution modulus kT. Following this analogy, taking the reasonable view that Q is large compared to W/n, the fraction of cells $\Delta n/n$ with strain energy greater than Q is given by

$$\frac{\Delta n}{n} = K \exp -nQ/W, K = 2(nQ/\pi W)^{1/2} \quad [1]$$

Since any changes in the coefficient K would be overwhelmed by the corresponding changes in the exponent, K may be regarded as a virtual constant. Q is not an activation energy.

The work of Taylor and Quinney[13, 14] shows that a metal's gross capacity to store energy saturates at large reductions in room temperature compression. It may be assumed that individual cells have a finite probability of becoming saturated for any deformation, and that the energy level Q lies close to the upper limit, if, indeed, it is not identical with it.

Up to this point each of the volume cells has been assigned an equal *a priori* probability of achieving the nucleation level Q. This assumption could only be justified for perfect single crystals. In polycrystalline materials, on which most investigations have been made, those cells encompassing a segment of a grain boundary appear to have a much greater probability of reaching the Q-level than similar volume elements in the grain interior. Two factors contribute to this statistical preference: 1—Grain boundary cells possess an initial strain energy, before deformation, by virtue of the lattice distortion in that region. 2—Slip propagation is inhibited at the grain boundaries, resulting in a concentration of residual strain in the adjacent volume elements.

For the simple case of a deformed single crystal, the number N_r of successful nucleations, or recrystallized grains per unit volume, should be proportional to the number Δn of cells which attain the near maximum energy level Q during deformation, or

$$N_r = a\Delta n = aKn \exp -nQ/W \quad [2]$$

where the proportionality coefficient α depends on both nucleation and growth rates of the new grains.[3] However, as Eastwood has pointed out,[15] if the activation energies for nucleation and for growth are the same, or nearly the same, α will not vary much with temperature. No pertinent data have been obtained for single crystals, but the existing data on polycrystals, discussed below, indicates that α is substantially independent of the temperature, over the range investigated. Thus N_r would be simply proportional to Δn, the latter quantity corresponding to the potential nuclei in the Avrami theory.

In the polycrystalline case, because of the statistical weighting that must be given to the grain boundary cells, it would be expected that the recrystallized grain count would depend not only upon W, as for single crystals, but also upon the initial grain boundary area per unit volume. No exact solution could be attempted unless the ratio of energy stored in the grain boundary regions to energy stored in the grain interiors could be estimated. By making use of the experimental observation that a great majority of nucleations do occur at grain boundaries, a reasonable approximation may be tried.

Assuming that a fraction $W_s = CW$ of the total stored energy is distributed among the n_s cells comprising the total initial grain boundary area A_s per unit volume, with the approximation that the probability of a successful nucleation at a grain boundary is overwhelmingly greater than that in a grain interior, Eq. 2 may be adapted to read, for a polycrystal

$$N_r = \alpha \Delta n_s = \alpha K_s n_s \exp -n_s Q/W_s \qquad [3]$$

For geometrical simplicity, it is stipulated that there are N_s cubic grains per unit volume before recrystallization, and N_r grains after. Using a more realistic space filling solid in place of the cube merely makes trivial changes in constants which are ultimately to be evaluated by experiment in any case. $N_s^{-1/3}$ then represents an average initial cube length, and may be taken as a convenient measure of the initial grain size G_s. Similarly, $G_r = N_r^{-1/3}$. The average initial area per grain is $3/N_s^{2/3}$, and the total initial grain boundary area per unit volume becomes $A_s = 3N_s^{1/3}$. This surface may then be divided into the n_s elements of area ΔA, so that $n_s = 3N_s^{1/3}/\Delta A$.

Taking the natural logarithms of both sides, Eq. 3 becomes

$$\ln G_r = (1/3) \ln MG_s + (D/G_s)\ (1/W_s) \qquad [4]$$

where $M = A/3\alpha K_s$ and $D = Q/\Delta A$ may be regarded as constants to be determined by experiment. An explicit dependence of the primary recrystallized grain size on the initial grain size, as well as on stored energy, is thus indicated. Since MG_s is a number always less than one, the first term will be negative, while the second is always positive. Thus Eq. 4 predicts a decrease in grain size with increasing deformation, i.e., increasing W_s, which is consistent with experiment. The singularity at $W_s = 0$ is of trivial significance.

Eq. 4, as it stands, represents an approximate phenomenological solution to the problem. Unfortunately, in the relevant constant temperature recrystallization experiments to date, the stored energy is not a measured quantity. Instead, the more easily determined fractional change in length along some axis of compression has been generally employed. In order to compare calculation with experiment, further approximations must be used to express W_s in terms of ν, the dimensional reduction as reported. It should be noted that these supplementary assumptions are the result of experimental, not theoretical, ambiguity, and do not prejudice the derived expressions in Eqs. 2 to 4.

Taylor and Quinney[13, 14] have shown that, up to about 70 pct reduction in compression, a rather definite fraction of the energy expended in deforming the material is retained as stored energy at room temperature. Granting that a considerable portion of this stored energy may be released upon heating, prior to recrystallization, the residual stored energy W_s might still be regarded as proportional to the work done in deforming the material.

Consider a unit cube compressed between frictionless parallel plates. The fractional reduction in L_s, the cube edge perpendicular to the plates, is denoted by ν, where $\nu = (L_s - L_f)/L_s$. Hence $L_f = L_s(1 - \nu)$. If the area in contact with the plates is A, the assumption of constant density leads to the relation $AL_s = A_fL_f = 1$. For the unit volume cube, the average area $\bar{A}$ in contact with the plates during the compression is then

$$\bar{A} = (A_s/2)\left\{1 + \left[\frac{L_s}{L_f}\right]\right\} = \tfrac{1}{2}A_s\left[\frac{2-\nu}{1-\nu}\right]$$

Letting σ represent the unit stress that must be exerted by the plates in order to cause plastic flow in the specimen, an average value $\bar{\sigma}$ may be approximated by $\bar{\sigma} = \sigma_s + \tfrac{1}{2}\epsilon\nu$. Here ϵ is regarded as an effective value of $d\sigma/d\nu$ over the measured interval.

The work done in deforming the specimen is then given by

$$W_d = \bar{\sigma}\bar{A}(L_s - L_f)$$

Relating this quantity to W_s by the undetermined proportionality factor β, and substituting the values obtained above for the other factors, there results

$$W_s = \frac{\beta}{4(1-\nu)}\left[4\sigma_s\nu + 2(\epsilon - \sigma_s)\,\nu^2 - \epsilon\nu^3\right] \qquad [5]$$

This expression could not be evaluated exactly without detailed information concerning ϵ, which is a measure of the work hardening, and which would depend upon the metal, the deformation temperature, and probably on the rate of deformation. Such detailed computation would hardly be warranted on the basis of the preceding assumptions, even if sufficient information were supplied for the experiments of present interest. Since ν is a quantity always less than unity, usually of order of magnitude 10^{-1}, it appears that a rough but sufficient approximation can be obtained by using only the first term of the polynomial in ν. This gives

$$W_s = \beta\sigma_s\left[\frac{\nu}{1-\nu}\right] \qquad [5a]$$

Substituting this into Eq. 4, the following is obtained:

$$\ln G_r = B + P\left[\frac{1-\nu}{\nu}\right] \qquad [6]$$

For a constant initial grain size, as in the experiments discussed below, the quantities $B = (1/3)$ $\ln MG_s$ and $P = D/G_s\beta\sigma_s$ may be regarded as the experimentally determined constants, or fitting parameters.

Table I. Data on Values of $-\log G_r$

ν	Data	Eq. 6	Eq. 7
0.15	2.020	2.015	2.024
0.30	2.100	2.105	2.095
0.38	2.130	2.130	2.125
0.60	2.200	2.171	2.201

Eq. 6 is now in a form suitable for comparison with the empirical relationship first established by Walker[19] for cartridge brass, and substantiated by the data of French[20] and Channon[21] for brass, Wensch[22] for commercial nickel, and Leighly[23] for commercial titanium. Walker's rule is normally written in the form

$$\log G_r = \log m + n(100\nu)^{1/2} \qquad [7]$$

where $\log m$ and n are constants for a given initial grain size, and ν ranges between 0.1 and 0.7 for the measurements involved.

Since the two constants are found to be negative in Walker's equation, both theoretical (Eq. 6) and empirical (Eq. 7) expressions predict a decrease in recrystallized grain size with increasing ν. The general statistical approach, as well as the supplementary assumptions involved in the derivation of Eq. 6, makes the results invalid for $\nu = 0$ or $\nu = 1$, so comparison at these points is not significant.

When fitted to recent data on titanium, in which Leighly[23] has observed that the recrystallization follows Walker's rule, the two expressions yield approximately equivalent results at low strains, as shown in Table I.

Similar, or somewhat better, correspondence may be obtained by fitting the data of Walker, French, Channon, or Wensch. Because of the additional assumptions involved in converting the percentage of deformation into stored energy, some disagreement would certainly be expected, even if all the theoretical assumptions were valid. However, the procedure adopted appears to be the best that can be done with the evidence at hand.

Since $\log G_r$ is a rather insensitive function of ν, the comparison with existing data cannot be said to prove that the relationship developed is correct. The calculation does permit one to say that Walker's rule, which is well substantiated in the ν range between 0.1 and 0.7, yields results which are consistent with the phenomenological stored energy considerations employed above.

Where the materials used in recrystallization experiments undergo extensive mechanical twinning, it might be expected that the G_r referred to in Eq. 4 should be the grain size just after deformation, not the initial grain size. Both theoretical and empirical expressions should probably be limited in their application to specimens in which the initial and final grain sizes are less than the least dimension of the specimen. In addition, neither could be expected to hold for constant time recrystallization experiments, in which the primary recrystallized grain size is materially altered by competitive grain growth.

Polygonization, as the writers have discussed it above, is by no means the only fragmentation hypothesis now extant. As early as 1914, Darwin[24] suggested the well-known mosaic block model for the structure of an annealed metal, and, more recently, Wood and Rachinger[25] have proposed that plastic deformation directly breaks the lattice into very small crystallites. In support of this model are the observations of Heidenreich,[26] who has noted structural segments of the order of 200Å on an edge in aluminum. Bragg[27] has employed this idea to calculate the mechanical strength of metals. Kellar, Hirsch, and Thorpe[28] also find small crystallites existing in deformed but unannealed aluminum.

Although mosaic blocks, polygonized segments, and Wood crystallites differ in the postulated formation mechanism, the ultimate structures seem to vary only in size and degree of orientation difference between fragments. This distinction may not be a fundamental one, i.e., the different nomenclature might very well describe different stages of the same phenomenon. It should be noted, however, that some time must elapse between the deformation of a metal and the taking of an X-ray picture. The fact that some crystallites are indicated by the X-ray evidence does not prove that these were formed simultaneously with the deformation.

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Magnetic Annealing of a Co-Fe Alloy

by A. H. Geisler, J. P. Martin, Eberhard Both, and J. H. Crede

The investigation of a 50 pct Co alloy was undertaken to determine whether there was any direct correlation between the structure and properties of Co-Fe alloys which were given various magnetic heat treatments. The magnetic anisotropy and texture of the 0.002-in. cold-reduced 98 pct material tend to decrease and change in nature with increasing temperature of the recrystallization anneal. Annealing samples in a magnetic field had little effect on either the magnetic properties or texture. However, cooling them in a magnetic field greatly improved their magnetic properties.

THE beneficial influence of a magnetic field applied during the heat treatment of certain soft magnetic materials has been known for a long time. Early work showed that the presence of a magnetic field of a few oersteds during the heat treatment of Fe-Ni alloys will cause a large increase in maximum permeability. A pronounced increase in the residual induction which is produced by the magnetic anneal causes the hysteresis loop to approach the shape of a rectangle. Such results are beneficial since the desired properties are high permeability, high induction at maximum permeability, high residual induction, and low coercive force. More recently Libsch and coworkers[1] studied the effect of magnetic annealing on the hysteresis properties of a series of Co-Fe alloys prepared from powders. They observed good response for the 35 and 50 pct Co alloys but little response for the 42 pct Co alloy. They pointed out that this was somewhat surprising since the 42 pct alloy has a high linear magnetostriction and zero crystal anisotropy and similar conditions in Fe-Ni alloys give excellent response to magnetic annealing. They found optimum properties to be at the 50 pct composition with residual induction, B_r = 19,000 gauss and coercive force, H_c = 0.68 oersteds after the magnetic anneal. Before the magnetic anneal these values were B_r = 12,600 gauss and H_c = 1.15 oersteds. The optimum treatment consisted of cooling from above the γ-α transformation temperature to 900°C in a field of 20 oersteds, holding 1½ hr at 900°C, then cooling at a rate of 20° to 25°C per min in the field to below 230°C. Cooling rate mainly affected coercive force with the value decreasing from 1.09 to 0.88 oersteds as the rate was increased from 3° to 48°C per min. Cooling from 1020° to 900°C in a field followed by further cooling to 230°C without the field gave properties decidedly inferior to those for samples annealed with the field applied throughout the cooling. They concluded that to get the best properties the samples must be cooled in a field to a threshold temperature above which the alloy is plastic enough to be affected by magnetostriction. In this respect the holding temperature must be high enough so that the alloy exhibits good plasticity to permit the optimum orienting of magnetic domains by relaxation of magnetostriction. In contrast, the holding time was of less significance for there was little improvement when the time exceeded ½ hr.

The improvement in properties effected by magnetic annealing has usually been attributed to the establishment of a domain texture caused by the "freezing in" of magnetic strains. On the other hand, Smoluchowski and Turner[2, 3] apparently found that a magnetic field applied during recrystallization could alter the crystal texture. If this effect is real, improved properties would also be expected when

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Table I. Analyses of Two Experimental Heats, Wt Pct

Samples	Co	C	Mn	P	S	Si
0.014 in.	50.59	0.023	0.51	0.008	0.020	0.052
All others	50.15	0.017	0.42	0.008	0.021	0.060

the applied field promoted the formation of a crystal texture with either an easy direction of magnetization or a direction of minimum magnetostriction in the field direction. Smoluchowski and Turner worked with a 35 pct Co alloy which they recrystallized at about 700°C. The normal recrystallization texture contained the following three main components:

R.D. = [110] R.P. = (100)

R.D. = 15° from [110] R.P. = (100)

R.D. = 15° from [110] R.P. = (111)

where R.D. is the rolling direction and R.P. is the plane of rolling.

The influence of the magnetic field appeared to be a strong enhancement of the [110] (100) component of the recrystallized texture at the expense of the other two components. Their hypothesis for this behavior is based on anisotropy of magnetostriction. The available data showed that the [110] direction is one of low magnetostriction. Thus nuclei with this direction in the field direction would involve less strain energy and would be favored for growth during magnetic annealing, which apparently was confirmed by the texture studies. Subsequent work[4] has shown that some of the previously published details need revision. When the influence of annealing temperature on the texture was considered it was found that the magnetic field suppressed the [110] (100) component to the contrary in favor of the other two previously mentioned components. Measurements on single crystals have shown that the magnetostriction in the [100] direction is low which conforms to the hypothesis of Smoluchowski and Turner based on anisotropy of magnetostriction. On the other hand, the more recent results thus do not exclude the alternate hypothesis that the texture is affected by virtue of a [100] direction of easy magnetization.

The present work was undertaken in order to achieve a direct correlation of the structure and properties of Co-Fe alloys. The work of Libsch, et al. reported no permeability measurements or texture data; that of Smoluchowski and Turner contained no measurements of properties. It would be desirable to make property measurements and texture analyses on the same samples in order to appraise the influence of thermal history.

Experimental Procedure

The results reported here refer to an alloy of nominal 50 pct Co composition. This alloy is of special interest since Libsch, et al. found that the 50 pct alloy exhibited good response to magnetic annealing, also an order-disorder reaction occurs in this composition at about 732°C.

Two experimental heats of the analyses given in Table I were involved. The first analysis applies to the 0.014 in. thick samples listed in Table II, the second applies to all other samples including those which were used for preferred orientation studies. The alloys were hot-rolled to about 0.10 in. thick and then were cold-rolled to the final thicknesses of 0.014 in. and less. The hot-rolled strip, which is extremely brittle, was rendered sufficiently ductile for cold rolling by rapidly quenching in iced brine from above the order-disorder transformation temperature. Texture studies were made on the 0.002 in. strip only since this thickness was most suitable for the transmission X-ray diffraction technique.

The variables which were investigated included annealing temperature, presence or absence of a direct current field of 20 oersteds during annealing, the cooling rate, the presence or absence of a field during cooling, the thickness of the sheet, and the action of reannealing. All thermal treatments were conducted in an atmosphere of dry hydrogen.

The magnetic tests were made on three types of ring-shaped samples. These included stamped round rings and stamped square window laminations both made by punching flat sheet, and wound toroidal cores made by coiling long lengths of narrow strip about a mandrel. The field during heat treatment and subsequently during testing was applied by passing an electric current through a coil of copper wire which was wound through each ring sample. Direct current magnetization and hysteresis measurements were made on a ring tester employing a Fahy control board. The anisotropy resulting from annealing at various temperatures between 454°C* and 980°C was measured by a spinning

* The temperatures in this investigation were measured in Fahrenheit degrees and converted to centigrade degrees. The accuracy of measurement was ±10°F.

Table II. Properties of the 0.014-In. Thick Strip*

Effect of Recrystallizing and Reannealing in Field

Entry No.	Annealing Conditions	Annealing Field	Cooling Rate	Cooling Field	Residual Induction, B_r x10^{-3}	Coercive Force, H_c	Maximum Permeability, $\mu_{Max.}$ x 10^{-3}	Induction at $\mu_{Max.}$ x 10^{-3}
1†	Recrystallized 2 hr 871°C	No	0.5°C per min	No	15.5	0.9	10	15
2†	Reannealed 2 hr 871°C	No	0.5°C per min	Yes	20.7	0.5	30	18
3	Recrystallized 2 hr 871°C	Yes	0.5°C per min	Yes	21.3	0.5	30	17.5
4	Reannealed 1½ hr 1260°C	No	0.5°C per min	No	17.1	1.6	6.8	15
5	Reannealed 18 hr 940°C	No	0.5°C per min	Yes	18.0	1.4	10	15.5
6	Recrystallized 18 hr 940°C	No	0.5°C per min	No	16.8	1.5	6.8	14
7	Recrystallized 5 hr 788°C	No	0.5°C per min	No	14.6	0.9	9	13
8	Reannealed 2 hr 788°C	No	Rapid	No	13.0	1.0	8.6	11
9	Recrystallized 1½ hr 871°C	Yes	Rapid	Yes	15.4	0.6	17	12.5
10	Reannealed ½ hr 593°C	Yes	0.5°C per min	Yes	19.8	0.5	26	16
11	Reannealed 1½ hr 704°C	Yes	0.5°C per min	Yes	20.9	0.5	30	17.5
12	Recrystallized 2 hr 871°C	Yes	Moderate	Yes	19.7	0.5	28	16.6
13	Reannealed 4 hr 593°C	Yes	0.5°C per min	Yes	21.1	0.45	34	19

* All data obtained on stamped ring specimens.
† See Fig. 1 for hysteresis loops.

disk test using 1.03 in. diam specimens of the 0.002 in. thick strip.

The preferred orientations of the as-rolled and recrystallized samples were determined with a General Electric XRD-3 X-ray diffraction spectrogoniometer by a previously described technique.[6] Since the grain size of the recrystallized samples was only moderately fine, it was necessary to develop a new specimen goniometer in order to permit scanning of an area of the sample. The device which has been briefly described previously,[5,6] reciprocates the sample through a 1 in. stroke past the X-ray beam so that an area of 1x0.3 in. (beam width) is covered in each stroke. At the same time the sample is rotated a fraction of a degree about an axis normal to its surface in synchronism with the movement of the chart recorder. Traces were made for increments of 5° about an axis in the surface of the sample from 0° to 60° starting from normal to the surface. This group of traces covers the major part of the pole figure. Corrections were made for the background of the traces and for the absorption of the samples. The results were plotted as pole figures with the contours of selected intensity levels in counts per second.

Results

Magnetic Properties: The results of the initial work which was conducted on 0.014 in. thick strip before texture studies were anticipated illustrate the influences of some of the annealing variables on the properties of the 50 pct Co alloy. A few of these results are listed in Table II. The first two entries illustrate the three-fold increase in maximum permeability obtained by cooling the sample in a magnetic field after it had been first recrystallized without an applied field. The hysteresis properties of these samples may be compared in Fig. 1. Comparison of the second and third entries shows that the properties for the sample recrystallized in the field (No. 3) are not superior to those of the sample which was recrystallized without the field (No. 2).

Table III. Effect of Thickness on Properties of Strip Recrystallized at 871°C*

Thickness, In.	Cold Reduction, Pct	Residual Induction, B_r x 10^{-3}	Coercive Force, H_c	Maximum Permeability, μ_{Max} x 10^{-3}	Induction, at μ_{Max} x 10^{-3}
0.014	86	20.0	0.33	39.0	14.6
0.006	94	19.2	0.45	28.0	15.2
0.002	98	16.9	0.62	16.7	12.0

* Recrystallized in field, cooled 0.5°C per min to 204°C in field, stamped ring samples.

These results indicate that any effect of an applied field during the initial recrystallization process is insignificant compared with the effect of cooling in the magnetic field. The fourth and fifth entries show that the good properties of entry 3 can be destroyed by heating to higher temperatures where grain size is increased and texture changed. In addition the results from entry 6 show that annealing at 940°C also gives poorer properties even though the material had not been annealed in the γ phase field. Entries 7 and 8 show that in the absence of an applied field two different cooling rates produce poorer properties, whereas entry 9 shows that when a field is applied even the rapid rate of cooling (about

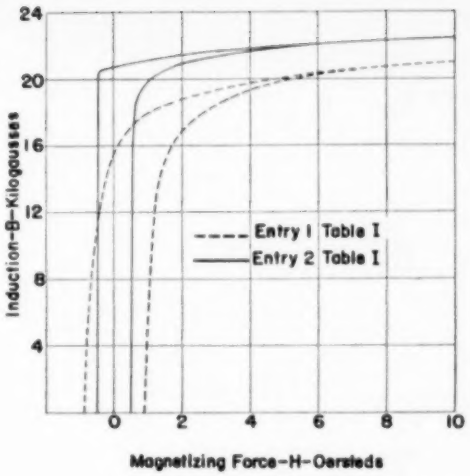

Fig. 1—Portions of hysteresis loops showing effect of magnetic anneal on 0.014-in. thick strip for peak magnetizing force of 100 oersteds. No field—Entry No. 1 in Table I. Field during cooling—Entry No. 2 in Table I.

33°C per min) gives better properties than slow cooling in the absence of the field. Comparison of the data for entries 10 and 11 with entry 9 illustrates that reannealing at lower temperatures followed by slow cooling in a field will provide good properties in material which initially had been cooled too fast. This is also shown by the data for entries 12 and 13 where the 4 hr anneal at 593°C promoted a well ordered structure according to superlattice lines in the X-ray diffraction pattern.

On the basis of these data it is apparent that the cooling conditions—rate and presence of a field—are of prime importance. The temperature at which the material is recrystallized is also important but the presence of a field during the recrystallization is not necessary to obtain optimum properties.

The optimum properties depend somewhat on the thickness of the strip according to the results in Table III. There seems to be a general trend toward poorer properties as the thickness of the strip is reduced below 0.014 in. While no attempt will be made to explain this trend which is related to the degree of final cold reduction, it should be realized that it exists and that the balance of the work to be reported was on 0.002 in. thick strip, the optimum thickness for X-ray diffraction studies.

In order to survey the effect of recrystallizing temperature and arrive at an optimum for the 0.002 in. thick strip, tests were made on samples that had been heat-treated at temperatures between 732° to

Table IV. Effect of Annealing Temperature on Properties of 0.002 in. Strip

Annealing Temperature, °C*	Residual Induction, B_r x 10^{-3}	Coercive Force, H_c	Maximum Permeability, μ_{Max} x 10^{-3}	Induction at μ_{Max} x 10^{-3}
732	19.6	0.78	16.5	16
760	20.5	0.64	25.5	17.6
788	19.7	0.59	21.6	16
816	20.2	0.55	27.6	16
871	19.9	0.68	18.7	15
927	19.5	0.53	27.4	16.4

* Held for 2 hr in field of 20 oersteds, cooled at about 0.5°C per min to 204°C in field. Wound toroidal samples.

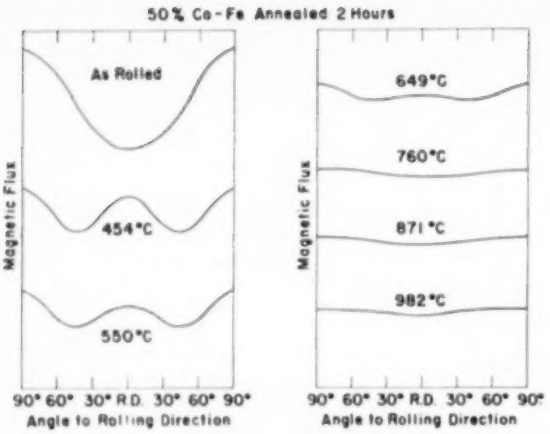

Fig. 2—Anisotropy of 0.002-in. thick strip annealed for 2 hr at indicated temperatures.

927°C. Properties are listed in Table IV. While there is some tendency for coercive force to decrease with increasing temperature, there is no clear trend in the properties for this range of temperatures. On the basis of the slightly higher residual induction value a temperature of 760°C was chosen for the subsequent studies of annealing treatments.

The variation of the anisotropy for various recrystallizing temperatures is shown by results from the spinning disk tests which are plotted in Fig. 2. The horizontal coordinate is the angular position around the disk starting from the transverse direction, moving to the rolling direction and then back to the transverse direction. The vertical coordinate is a relative value for the change of flux in the disks plotted on the same scale for all curves. Maxima and minima are related directly to the permeability. Thus, the best permeability direction is at 90° to the rolling direction in most cases but with minima in the rolling direction for the as-rolled sample and those recrystallized at 760° to 982°C and minima at about 45° to the rolling direction for samples recrystallized at 454° to 649°C. Little anisotropy remains for the samples recrystallized at 760°C or above. The origin of the variation in anisotropy will be evident when the results of texture analyses are discussed later.

The properties of the samples used for texture studies are listed in Table V. Each group includes two or three types of specimens. The first entry in each group refers to a wound toroid of ¼ in. wide strip on which magnetic tests were made. The second entry refers to a core of 1 in. wide strip which was wound on a mandrel of square cross section and annealed with the first entry and used for texture studies. The texture specimens were cut from the 1½ in. long flat sides of the wound cores. Third and fourth entries refer to stamped square laminations with samples taken from two legs, one where the applied field was parallel (W) to the direction of rolling and the second where the field was across (X) the direction of rolling. While the texture components will be discussed later, the relationships between properties and thermal treatment can be compared with those for heavier gage. Again the improvement in properties afforded by cooling in a magnetic field is apparent. When the field was applied during cooling (groups 1 and 3) good properties were obtained and when no field was applied during cooling (groups 2 and 4) poorer properties were obtained regardless of whether or not a field was applied during recrystallization. In these respects the behavior was similar to that for heavier gage strip, Table II. On the other hand, holding at 593°C to promote a well ordered structure (group 5) did not increase the maximum permeability, while rapid cooling (group 6) did not have as detrimental an effect as with the heavier gage strip. The poorest properties were obtained with rapid cooling without an applied field (group 7).

Preferred Orientations: The texture of the original cold-rolled strip is of interest in explaining the recrystallization texture; it is the same as that of cold-rolled iron and is shown by Fig. 3. Various

Table V. Properties and Textures of 0.002 In. 50 Pct Co Strip Recrystallized 2 Hr at 760°C

	Recrystallization		Cooling							
Group	Field	Direction	Field	Rate	Residual Induction, $B_r \times 10^{-4}$	Coercive Force, H_c	Maximum Permeability, $\mu_{Max.} \times 10^{-3}$	Induction at $\mu_{Max.} \times 10^{-4}$	Texture Components*	
1	Yes	W	Yes	0.5°C per min	19.8	0.6	23	15.7	—	
	Yes	W	Yes	0.5°C per min	—	—	—	—	5 pct *DE*	See Fig. 4a
	Yes	W	Yes	0.5°C per min	—	—	—	—	10 pct *A*	
	Yes	X	Yes	0.5°C per min	—	—	—	—	15 pct *A*	
2	Yes	W	No	0.5°C per min	16.9	0.8	13	12.1	—	
	Yes	W	No	0.5°C per min	—	—	—	—	10 pct *DE*	See Fig. 4b
	Yes	W	No	0.5°C per min	—	—	—	—	20 pct *A*	
	Yes	X	No	0.5°C per min†	—	—	—	—	20 pct *A*	
3	No	W	Yes	0.5°C per min	19.5	0.7	20	16.2	—	
	No	W	Yes	0.5°C per min	—	—	—	—	5 pct *A*—5 pct *DE*	See Fig. 5a
	No	X	Yes	0.5°C per min	—	—	—	—	10 pct *A*	
4	No	W	No	0.5°C per min	16.1	1.2	9	12.4	—	
	No	W	No	0.5°C per min	—	—	—	—	20 pct *A*—10 pct *DE*	See Fig. 5b
5	Yes	W	Yes	0.5°C per min†	20.6	0.9	18	16.5	—	
	Yes	W	Yes	0.5°C per min†	—	—	—	—	20 pct *A*—5 pct *DE*	See Fig. 7a
	Yes	X	Yes	0.5°C per min†	—	—	—	—	35 pct *A*—5 pct *DE*	
6	Yes	W	Yes	33°C per min	18.1	0.7	19.5	13.5	—	
	Yes	W	Yes	33°C per min	—	—	—	—	30 pct *A*—5 pct *DE*	See Fig. 6a
	Yes	X	Yes	33°C per min	—	—	—	—	25 pct *A*	
7	No	W	No	33°C per min	15.3	1.2	7.3	11	—	
	No	W	No	33°C per min	—	—	—	—	15 pct *A*—5 pct *DE*	See Fig. 6b

* In addition to the pure 760°C recrystallization texture which contains only components spread from H to K. The deformation texture corresponds to the spread from A to G.
† Held 4 hr at 593°C.

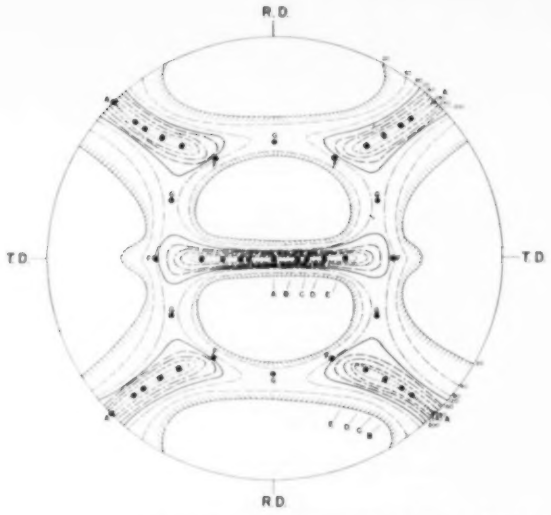

Fig. 3—Pole figure for cold-rolled 50 pct Co-Fe strip of 0.002-in. thickness showing distribution of (100) poles in stereographic projection.

components which contribute to the deformation texture are indicated by the letters *A* to *G* and are identified in Table VI. The main part of the texture can be defined as a continuous spread from (001) (*A*) to (111) (*F*) in the rolling plane about a [110] direction in the rolling direction. There is almost an equal distribution from (001) to (112) (*E*) in the rolling plane. The component between *F* and *G* which has a [111] direction in the rolling direction is present in moderate amounts with an intensity above 80 counts per sec. Since the [111] direction is the direction of easy magnetization in this alloy,[7] it might be expected that a possible effect of a field applied during recrystallization would be to intensify this component.

Table VI. Components in Textures of Co-Fe Alloys

A.	(001)	[110]	*H.*	(001)	[120]
B.	(11$\bar{7}$)	[110]	*J.*	16° (001)	16° [120]
C.	(115)	[110]	*K.*	(322)	[315]
D.	(11$\bar{3}$)	[110]	*L.*	(311)	2° [315]
E.	(11$\bar{2}$)	[110]	*M.*	4° (221)	6° [221]
F.	(111)	[110]	*N.*	3° (112)	9° [211]
G.	(11$\bar{1}$)	[112]			

Pole figures for eight of the samples which had been recrystallized by annealing for 2 hr at 760°C are shown in Figs. 4 to 7. The main features of the texture are substantially different from those of the rolled texture. The components which spread from *H* to *K* and *L* in Fig. 4 are mostly complex as listed in Table VI. The main component, *H*, is the simplest because a (001) plane is in the rolling plane and a [120] direction is in the rolling direction. Under these conditions [100] directions are at 27° to the rolling direction and [110] directions are at 18° to the rolling direction. Evidently this is the component which was designated (100) 15° [110] by Smoluchowski and Turner.

On the whole there is little significant difference between the pole figures for samples recrystallized in a field, Fig. 4, and those recrystallized without an applied field, Fig. 5. There appears to be no concentration of intensity about the arcs which correspond to [111] directions in the rolling direction which was also the field direction. The same is also true of rapidly cooled samples, Fig. 6. On the other hand, in addition to the main components there appear to be minor and spurious portions of the texture which are described by the components *A* to *E* in Figs. 4 to 7. These are components of the rolled texture, Fig. 3, and also dominant components of the recrystallization texture for annealing at temperatures below 760°C according to the summary in Table VII. Although the extent of these minor portions of texture in the pole figures for samples annealed at 760°C varies among the samples, there appears to be no clear correlation with the annealing variables. Semiquantitative measurements of the minor components relative to the major ones are listed on the right side of Table V for the various combinations of annealing variables. Comparison of results for groups 1 and 2 with 3 and 4 shows that when the annealing was performed either with or without an applied field the amounts of minor components were in both cases 5 to 20 pct *A* and 5 to 10 pct *DE*. The latter is a component between *D* and *E* as measured on a goniometer trace for an angle 20° to the normal of the strip surface. It is also noteworthy that samples with relatively good properties can have either large amounts of the minor components (groups 5 and 6) or small amounts (groups 1 and 3). There appears to be some variation in amounts between samples within the groups of Table V. This variation among samples having the same treatment is more evident from the results given in Table VIII. Some adjacent samples taken from two annealed cores were examined and an attempt was made to reduce or remove the minor components by additional annealing at about 760°C. The results show that while the *DE* component remains about the same in samples from each core the quantity of component *A* varies considerably from one sample to the next adjacent in the core. Also additional annealing of the same samples at a slightly higher temperature tended to reduce the amount of component *A* but had little effect on component *DE*. These uncontrollable variations would make questionable any attempted correlation with annealing variables.

Finally, comparison of the texture for rapidly cooled samples, Fig. 6, with that for samples held at intermediate temperatures for time periods longer than that permitted during the slow cool (0.5°C per min) shows that the new minor components *M* and *N* of Fig. 7 develop during holding. These have been attributed to a supplementary recrystallization reaction which is evident from the microstructure and which is promoted by strains accompanying the ordering process.[8] The reaction occurs subsequent

Table VII. Occurrence of Various Components in Texture for Different Annealing Temperatures

Annealing Temperature, °C	Components	
	Predominant	Others
As-rolled	*A,B,C,D,E*	*F,G*
427	*A,B,C,G*	*D,E,H*
538	*A,B,C,G*	*D,H*
649	*A,B,C,G,H*	
760	*H,J*	*K,L*
871	*J*	*H,L*
982	*L*	*G,K*

See Table VI for descriptions of the components.

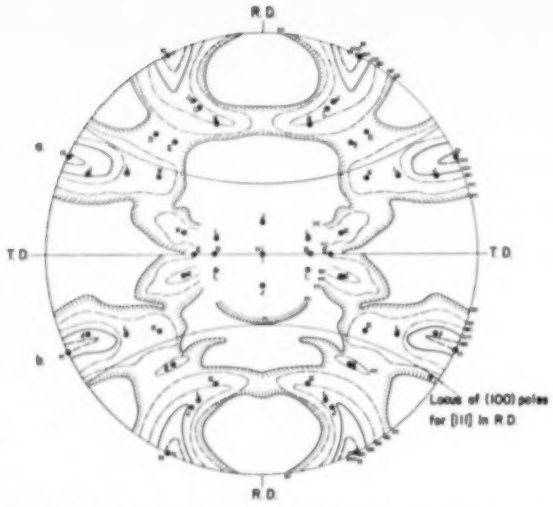

Fig. 4—Pole figures for samples recrystallized by annealing 2 hr at 760°C.
a—Annealed in field and cooled 0.5°C per min in field.
b—Annealed in field and cooled 0.5°C per min without field.

to the ordering process since cooling at 0.5°C per min develops a well ordered structure without the appearance of components *M* and *N*.

Discussion

The type of crystal texture developed on recrystallizing the 50 pct Co alloy is very strongly dependent upon annealing temperature, Table VII. At temperatures of 649°C and less, components which were in the rolling texture (*A* to *G*) persist and some of these, notably *G* $(11\bar{1})$ [112], are strongly enhanced. Starting at 427°C or less the *H* component (001) [120] attains increasing prominence and at 760°C it is the main component while those similar to the rolling texture have essentially disappeared. At still higher temperatures other components gain prominence but at the same time the texture levels out. On annealing at 982°C detectable but not pronounced texture persists. The nature of the magnetic anisotropy as shown by the spinning disk curves, Fig. 2, can be directly correlated with the texture type and its variation with temperature. Since [111] is the direction of easy magnetization in the 50 pct Co alloy, peaks corresponding to higher permeability will occur at peripheral positions around the disk where a [111] is in the rolling plane. The maxima in the as-rolled sample originate in component *E* which has a [111] in the transverse direction. This fact also accounts for the maxima in the transverse direction for samples annealed at 427° to 649°C. The maxima in the rolling direction for the latter samples are related to a component of the type (112) [111] which is near to the enhanced *G* component. With increasing annealing temperature the anisotropy diminishes as the *H* component is enhanced and at 760°C and above little anisotropy remains because there are few crystals with a [111] in the rolling plane. The similarity of the disk test results for annealing at temperatures above 649°C probably accounts for the uniformity of the magnetic properties on annealing in the range 760° to 927°C in Table IV.

Table VIII. Effect of Sampling and Repeated Annealing on Minor Texture Components

	Pct Component*	
	A	*DE*
Recrystallized 2 Hr at 760°C in Field, Cooled 0.5°C per Min. No Field		
Sample No. 1	0	10
Sample No. 2	20	10
Sample No. 3	15	10
Sample No. 3 reannealed 24 hr at 771°C	10	10
Sample No. 4 reannealed 24 hr at 754°C	15	10
Sample No. 5 reannealed 24 hr at 771°C	10	10
Recrystallized 2 Hr at 760°C in Field, Cooled 33°C per Min in Field		
Sample No. 6	30	5
Sample No. 7	10	5
Sample No. 7 reannealed 24 hr at 771°C	5	5
Sample No. 8 reannealed 24 hr at 754°C	10	5
Sample No. 9 reannealed 24 hr at 771°C	5	5
Above—repeated X-ray trace	5	5

* These are also components of recrystallization texture for lower annealing temperatures. Component *A* measured from 0° trace and *DE* from 20° trace.

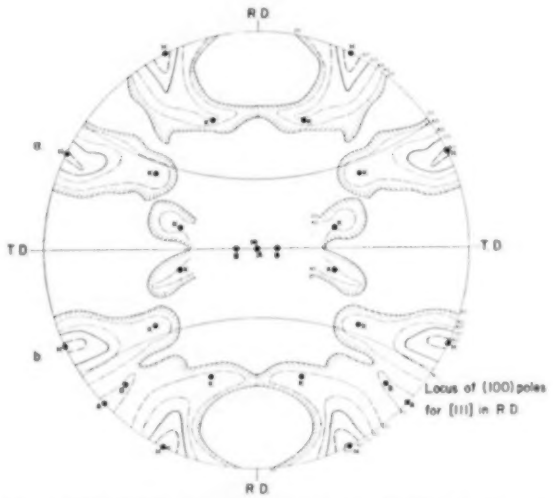

Fig. 5—Pole figures for samples recrystallized by annealing 2 hr at 760°C.
a—Annealed without field and cooled 0.5°C per min in field.
b—Annealed without field and cooled 0.5°C per min without field.

Both magnetic tests and texture studies failed to show any effect of an applied field on recrystallization during annealing of the 50 pct Co alloy at 760°C. This result is not surprising for there is no strong component in the rolled texture with the [111], the direction of easy magnetization, parallel to the field applied in the rolling direction. Thus, there could be little enhancement effected by the field if anisotropy of magnetization is the responsible factor. On the other hand single-crystal magnetostriction data are not yet available for the 50 pct Co alloy so the hypothesis of Smoluchowski and Turner which associates the effect in the 35 pct Co alloy with anisotropy of magnetostriction cannot be tested. On the other hand, there is a strong component *E* in the rolling texture with [111] in the transverse direction but tests failed to show that even this component was retained or enhanced by an applied field. First, a field would be operative in this direction on two sides of square laminations, but there was no increase in the *DE* component for cross (*X*) over with grain (*W*) sides of the squares according to Table V, and there was no improvement in the magnetic properties of square lamina-

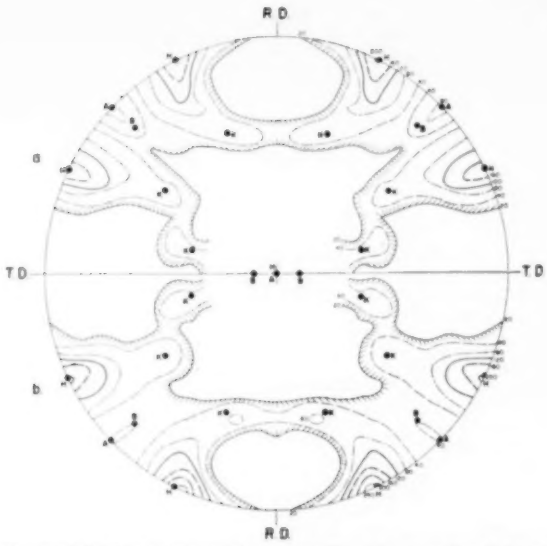

Fig. 6—Pole figures for samples recrystallized by annealing 2 hr at 760°C.
a—Annealed in field and cooled 33°C per min in field.
b—Annealed without field and cooled 33°C per min without field.

tions over wound cores. Second, there were no differences in the texture of simultaneously annealed disk samples in a series which was prepared so that the orientation of the field varied by increments of 5° from 0° to 90° to the rolling direction. Thus, the conclusion seems warranted that a field applied during the recrystallization of the 50 pct Co alloy at 760°C has no effect although cooling in a field after recrystallization does have a marked effect on properties.

The response of the 50 pct Co alloy to magnetic annealing at 760°C does not occur by virtue of a change in the overall crystal texture but by virtue of some change which occurs during cooling in the field subsequent to recrystallization. The nature of this change can only be postulated. At least two phenomena could be operative. First, the applied field could be promoting a preferred domain texture according to the older idea that the strains caused by the magnetic field are relieved by plastic flow in the alloy. In this way those [111] directions in the polycrystalline aggregate which are most nearly parallel to the applied field become directions of easiest magnetization. In each crystal the direction of spontaneous magnetization after a magnetic anneal will be the one preferred out of four <111> directions and in a sense a preferred domain texture exists in the aggregate. The other possibility is that the applied field causes preferential nucleation of certain orientations of particles of the ordered phase in the recrystallized, disordered matrix much the same as an applied field affects the transformation in the case of certain precipitation alloys such as Alnico 5. Perhaps it is not only coincidental that both Co-Fe and Ni-Fe alloys order at a sufficient rate in the temperature range where the applied field is effective so that consideration must also be given to the ordering reaction in these alloys. The disregistry between the lattices of the ordered and disordered phases in both these alloys is very low, a condition which seems to be necessary for effective magnetic annealing of precipitation alloys. Nucleation of coherent particles of the ordered phase in the disordered matrix involves strains which would be expected to lead to an intermediate tetragonal crystal structure and anisotropic shape for particles of the ordered phase. Preferential nucleation of a select orientation of the tetragonal axis and concurrent shape orientation from the several possible in each matrix crystal would arise by virtue of anisotropy energy decreasing the free energy required to nucleate the preferred orientation. If the prominent type of anisotropy energy is that of strain, then the process would embrace relaxation of magnetostriction by a permanent retention of the slight tetragonality imposed at the intermediate state by coherency much as outlined by the older interpretation.

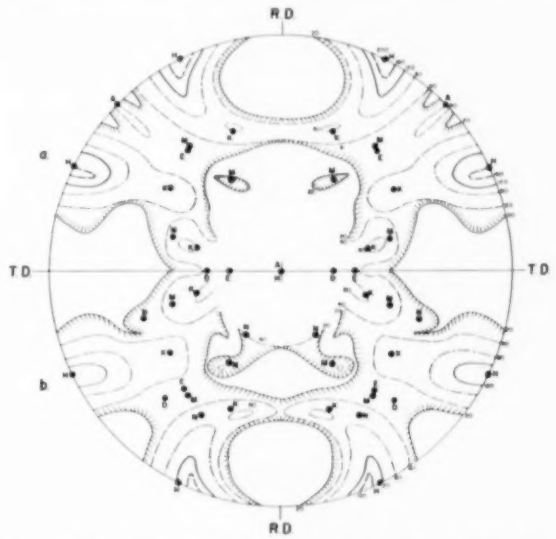

Fig. 7—Pole figures for samples held during cooling in field after recrystallizing for 2 hr at 760°C in field.
a—Held for 4 hr at 593°C.
b—Held for 10 hr at 600°C.

In either case whether the effects of magnetic annealing originate in domain texture or in the ordering process, if such a distinction can be made, even better properties would be expected if a preferred crystal orientation could be developed with a direction of easy magnetization in the applied field direction.

Summary

1—The presence of an applied magnetic field during recrystallization of a 50 pct Co-Fe alloy does not effect a significant change in either the magnetic characteristics or the recrystallized texture.

2—Improved magnetic properties, characterized by a rectangular hysteresis loop, result from cooling a recrystallized 50 pct Co-Fe alloy in the presence of an applied magnetic field from a temperature above 550°C.

3—The optimum temperature of recrystallization when followed by cooling in the presence of an applied magnetic field is dependent upon the thickness of the strip and thus is probably related to the degree of final cold reduction.

4—The magnetic anisotropy and texture of 0.002 in. thick strip cold-reduced 98 pct are strongly dependent upon the temperature of the recrystallizing anneal; they change and tend to decrease with increasing temperature until little magnetic anisotropy is apparent after a 760°C anneal although some preferred orientation is still present after a 982°C anneal.

5—Better magnetic characteristics are developed when an alloy of this composition is cooled slowly than when cooled rapidly regardless of whether or not a field is applied, but cooling at the faster rate of 33°C per min in an applied field gives better properties than cooling at 0.5°C per min without an applied field.

6—Optimum properties can be recovered by reannealing and cooling slowly in an applied field provided that the prior recrystallization had been performed at a proper temperature but regardless of whether or not the initial cooling had been at a slow rate in a field.

7—Reannealing below the ordering temperature results in a supplementary recrystallization reaction subsequent to the ordering process which is believed to be promoted by strains accompanying the ordering process.

8—A possible role of ordering in promoting the domain texture is discussed.

Acknowledgment

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Technical Note

Concentration Gradients Associated with Growing Pearlite

by Richard E. Grace

WHEN an Fe-C alloy, partially reacted to pearlite, is quenched rapidly enough to suddenly stop the growth process, it may be expected that any carbon concentration gradients will freeze *in situ* in the newly formed martensite. A short tempering treatment should precipitate finely dispersed iron carbide particles in approximately the same distribution in which carbon existed during the growth process. Examination with the electron microscope of areas of tempered martensite adjacent to the pearlite-martensite interface should reveal the existence of preferred areas of precipitation. Fig. 1 is an example of an electron micrograph used in this study.

Small sections of a commercial steel (0.9 pct C, 1.6 pct Mn, 0.25 pct Si) were austenitized at 945°C in air for 45 min, furnace-cooled to 697°C, isothermally reacted to pearlite for 30 min, and quenched into iced brine. Two samples were tempered 5 and 20 min, respectively, in air at 498°C and were subsequently quenched in water. The samples were mechanically polished and etched in 1 pct picral. Collodion replicas were made by the conventional technique; these were shadowed with chromium at about 650° from the horizontal, and electron micrographs were taken at a linear magnification of 14,200X. Prints were made at a magnification of 44,100X.

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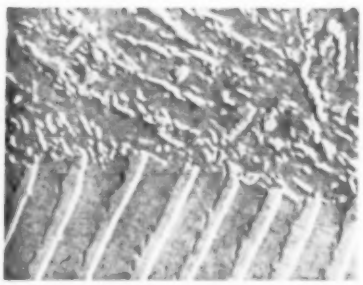

Fig. 1—Electron micrograph of pearlite and martensite tempered 5 min, 0.09 pct C steel. X20,000.

Lineal analysis of the prints was made as a function of the interlamellar spacing and volume percent of iron carbide. Straight lines were drawn into tempered martensite between adjacent lamellae at a distance $S/4$ or $S/6$ apart, where S is defined as the interlamellar spacing measured at the pearlite-martensite interface. The volume percent of iron carbide was measured along each of these traces with a "gage length" of $S/10$. The results of analyses of two samples are shown in Table I. The area included between the $S/2$ and S distance from the interface could be considered homogeneous within the sensitivity of the measuring technique. This value was used as a proportionality factor to evaluate an arbitrary carbon content of homogeneous austenite, and also as a parameter by which error in measurements could be evaluated. Results of the lineal analysis are shown in Figs. 2 and 3.

Fig. 4 shows the statistical nature of the interlamellar spacing for all lamellae measured in this

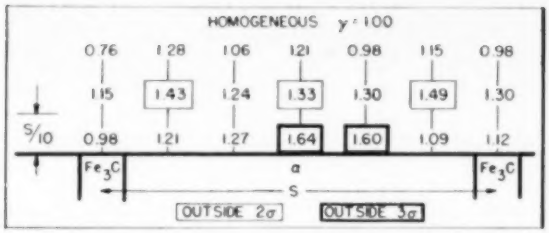

Fig. 2—No. 56b. Map of carbon concentrations preceding an advancing pearlite interface. OUTSIDE 2σ OUTSIDE 3σ show statistically important areas in these measurements.

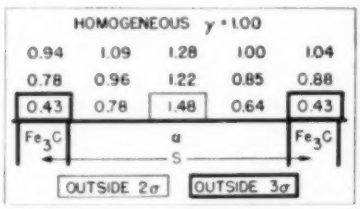

Fig. 3—No. 58b. Map of carbon concentrations preceding an advancing pearlite interface. OUTSIDE 2σ OUTSIDE 3σ show statistically important areas in these measurements.

Table I. Analyses of Two Samples

Sample	
56b	Tempered 5 min, 498°C; 51 lamellae measured; Volume percent carbide measured within pearlite = 37 pct; Volume percent carbide measured within homogeneous tempered martensite, mean = 33 pct (σ = 5.3 v/o, N = 35)*
58b	Tempered 20 min, 498°C; 39 lamellae measured; Volume percent carbide measured within pearlite = 34 pct; Volume percent carbide measured within homogeneous tempered martensite, mean = 29.5 pct (σ = 5.4 v/o, N = 25)

* $\sigma = \left(\frac{\Sigma\Delta^2}{N}\right)^{1/2}$ where σ is the standard deviation from the arithmetic mean; Δ, the difference between volume percent measured and the arithmetic mean at each site between $S/2$ and S from the interface; and N, the number of sites between $S/2$ and S from the interface.

study. Center-to-center distances of adjacent carbide lamellae were measured at the interface of randomly selected pearlite colonies. The data are grouped about certain discrete points corresponding to 0.10-in. intervals in the measuring technique.

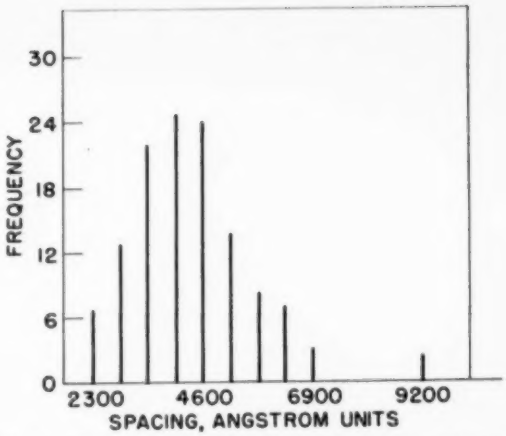

Fig. 4—Distribution of interlamellar spacings of No. 56b and No. 58b.

It does not appear that gross composition changes occur in austenite more than a fraction of an interlamellar spacing ahead of the growing pearlite colony. As tempering proceeds, the small carbides in front of the carbide lamellae will disappear in favor of the large lamellae. This may account for the very low carbon areas in Fig. 3. In general, this measuring technique is also applicable to the determination of the interlamellar spacing of pearlite. Etching and shadowing make carbide lamellae appear wider than their true width; but this should not affect careful lineal analysis, provided that the particle size distribution remains constant and only relative results are required.

Acknowledgment

The author wishes to thank A. L. Ellis for the use of the electron microscope at Manufacturing Research, International Harvester Co., Chicago; T. L. Thourson for taking the necessary electron micrographs; and Cyril Stanley Smith for his interest in this problem. This research was carried out at the Institute for the Study of Metals, University of Chicago under a grant from the Office of Ordnance Research, Contract No. DA-11-022-ORD-834.

Technical Note

Importance of the Iron Content of High-Purity Aluminum

by M. Metzger and J. Intrater

IN the large number of important studies on high-purity aluminum (e.g., recrystallization and grain growth, creep, internal friction), it does not seem to have been generally recognized that the iron content, despite its very low figure, has a strong influence on a number of properties. In part, its influence is due to the very low solubility of the Fe-Al θ phase. For aluminum of about 99.99 pct purity, the iron content may be 0.001 to 0.004 pct. For values in this range, a second phase will be present below 410° to 480°C. This was determined by extrapolation of a log solubility vs inverse temperature plot of the solid solubility data of Edgar.[1] One consequence is the inhibition of grain coarsening below the solubility limit. This is shown in Table I, which gives, for three iron contents, the annealing temperature required for the absence of grains smaller than ½ mm average diameter together with the minimum temperature for the presence of some grains larger than 2 mm diameter. The specimens were ¼x1½-in. strips cut from hard-rolled 1/16-in. sheet supplied by the Aluminum Co. of America.

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TN 162E. Manuscript, March 9, 1953.

Table I. Effect of Annealing Temperature on Grains

Fe, wt pct	0.0004	0.004	0.023
Minimum temperature for absence of grains smaller than ½ mm, °C	450	500	600
Minimum temperature to produce some grains larger than 2 mm, °C	Less than 400	450	550
Solution temperature, °C	375	480	590

They were annealed at 50°C intervals starting at 300°C (no test at 350°C). The schedule of heating times follows that of Edgar, who used times of 24 hr at about 650°C and extended the annealing period by 24 hr for each 50°C below this temperature.

These tests were performed in connection with a study of the effect of iron on the intergranular corrosion of high-purity aluminum in hydrochloric acid. The experimental technique essentially consists of observing the rates of intergranular corrosion of aluminum of different iron contents after quenching from various temperatures within the solid solution range. It is found that aluminum of a given iron content treated at one temperature behaves like material of higher iron content at a higher temperature. The results indicate that the iron in solid solution has a strong tendency to segregate at the grain boundaries, probably because at sites in the boundary where the lattice is locally "compressed," stress can be relieved when the aluminum atoms are replaced by the smaller iron atoms. The reasoning follows that of Cottrell[2] and of McLean.[3]

Considering the simple model of solute atoms distributed among regions of different potential energy, the concentration, c, of solute atoms in the boundary (i.e., in the transition region several atomic spacings thick between adjacent grains) will depend on the average concentration, c_o, according to the relation

$$c = c_o \exp(-E/kT) \qquad [1]$$

where E is the energy of interaction of the solute atom at the boundary site. For various sites, the value of E would be more negative for those at which the interaction is stronger. For iron in aluminum, the effective E determined by comparison of the results of corrosion experiments for different iron contents and temperatures is about −0.7 electron volt. This large energy is believed to indicate that the concentrations of iron in the boundary to which the corrosion test is sensitive are those which occur at the region in the center of the boundary where the lattice is highly distorted.

With an interaction energy of this magnitude for all grain boundary sites, Eq. 1 could hardly be valid, since it would indicate an excessive concentration of iron atoms at the boundary except at temperatures near the melting point. It is more likely that a progressive saturation of available boundary sites occurs as the temperature goes from just below the melting point, where only sites for which E is very large are occupied by iron atoms, to lower temperatures where sites of lower interaction energy can be occupied. Even with an iron content of order 0.001 pct, a large proportion of the boundary sites for which the interaction energy of an iron atom is comparatively high would be occupied at temperatures below 500°C. A saturation effect is also suggested by some of the experimental results.

Additional solute elements of smaller atomic diameter than aluminum would then be in competition with iron atoms for boundary sites. It is supposed that the atoms of an element which has less tendency to concentrate in the boundaries than has iron will have a lower interaction energy at any given site. The atoms of such an element could then occupy relatively few sites not already taken by iron atoms even if the element were present in somewhat larger amounts. Thus, substantial modification of the properties of the grain boundaries by the segregation of other alloying elements in solid solution would be produced only by elements which either have effective atomic diameters less than that of aluminum, but have stronger segregation tendencies than iron, or which have larger effective atomic diameters than aluminum and thus can segregate to the "expanded" boundary positions which the smaller iron atoms would not occupy.

On this basis, it is possible to explain the results obtained by Starr, Vicars, Goldberg, and Dorn[4] on the effects of alloying elements on the activation energy for grain boundary relaxation in aluminum as measured with the torsion pendulum. They found no significant effects for additions of zinc, silver, copper, and germanium, but there was an increase in the activation energy from 38,000 cal per mol in high-purity aluminum to 54,000 cal per mol for 1.617 atomic pct Mg. The alloys used contained 0.003 to 0.006 pct Fe and the temperatures of measurement ranged up to 500°C. It would therefore be expected, as indicated above, that the boundary sites most favorable for occupation by foreign elements of effective atomic diameter smaller than aluminum would have been taken up by iron atoms before any other elements were added. In the case of copper, relatively strong segregation would ordinarily be expected on the basis of its atomic diameter, which is considerably smaller than that of aluminum, but our corrosion experiments suggest that its tendency to segregate is slightly less than that of iron. Thus, only for additions of magnesium and (to a lesser extent) germanium, which have atoms larger than aluminum, would a considerable quota of grain boundary sites be available to the solute atoms.

Iron may produce an additional complication in experiments of this kind if the second phase exists as a precipitate in the grain boundaries and produces a restraining action on the relaxation of stress across the boundary.

The evidence of the authors and that of Starr et al. shows that, even in relatively pure aluminum, the behavior of the grain boundaries is strongly influenced by small amounts of other elements and that quantitative data obtained at temperatures considerably below the melting point should not be considered as good approximations to the values characteristic of the boundaries in the ideally pure metal.

The work out of which these observations grew was performed under contract Naw-6223 for the National Advisory Committee for Aeronautics to which the authors' thanks are due for permission to publish this note. An account of this work will be issued.

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Order-Disorder Transformation in Cu-Au Alloys Near the Composition CuAu

by J. B. Newkirk

Results of a Debye-Scherrer X-ray investigation are given which show that the order-disorder transformation is a first-order or heterogeneous reaction in Cu-Au alloys with compositions near CuAu. Evidence was found for conventional tie-line segregation across a usual type of two-phase field separating the ordered and disordered fields in the Cu-Au equilibrium phase diagram. The horizontal and vertical widths of the two-phase fields are about 3 atomic pct and 20°C, respectively, at 43 and 54 atomic pct Au. No evidence for the existence of an ordered structure based on a stoichiometric composition of Cu_3Au_2 could be found.

ALTHOUGH the modern theories relating the degree of order of binary alloys to temperature and composition have met with considerable success, the nature of the transformation from the disordered state to the ordered state and vice versa has never been well understood. It has been assumed by some[1] that this is a second-order transformation, that is, a homogeneous change of state. Others[2] hold that the transformation is first-order and that the effects characteristic of heterogeneous phase transformation apply. Since this subject is discussed in detail in a recent paper,[2] the arguments will not be repeated here.

The present paper summarizes an experiment which was designed to distinguish between these two viewpoints for the case of Cu-Au alloys near the composition CuAu. The Cu-Au system is an important one because it furnishes prototype alloys, the behavior of which has formed the basis of much of the present-day order-disorder theory. It has recently been shown[2] that in alloys near Cu_3Au there is a temperature range within which the ordered and disordered states coexist in equilibrium and are distinguishable as separate phases. Therefore, the transformation must be first-order for these alloys. A similar demonstration for alloys near CuAu, however, has been lacking.

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Discussion on this paper, TP 3537E, may be sent, 2 copies, to AIME by Dec. 1, 1953. Manuscript, Jan. 24, 1953. Cleveland Meeting, October 1953.

Experimental Method

Essentially the experiment consisted of equilibrating Cu-Au samples at various temperatures, quenching them in water to retain the high temperature states, and then examining them at room temperature for the coexistence of the ordered and disordered structures. The thermal gradient method of heat treatment[3] was used because it was important that all temperatures over the transformation range should be represented in the test. Briefly, this method consisted of holding a wire of the desired composition, sealed under vacuum in pyrex, in a known temperature gradient for a long enough time to allow each part of the wire to assume the crystal structure characteristic of the temperature at which it was held.

The temperature gradient was produced by inserting into an ordinary wire-wound cylindrical laboratory furnace, an 18 in. length of ⅛ in. ID ceramic tube which was heavily wrapped with asbestos. The furnace power was controlled by a Tagliabue Celectray controller and a chromel-alumel thermocouple with the junction located on the heating elements. During the equilibrating treatment the widest variation of temperature within the gradient tube was approximately 4°C at the highest temperature. The temperature at various places within the tube was determined, before inserting

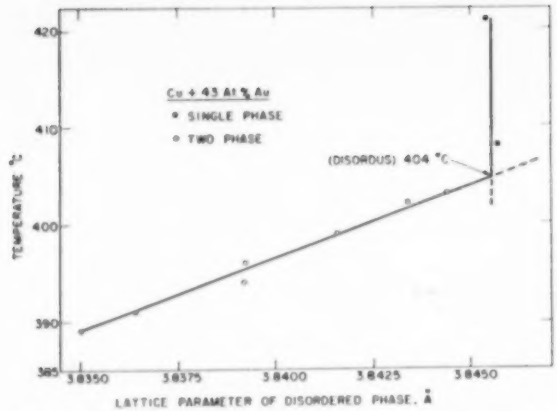
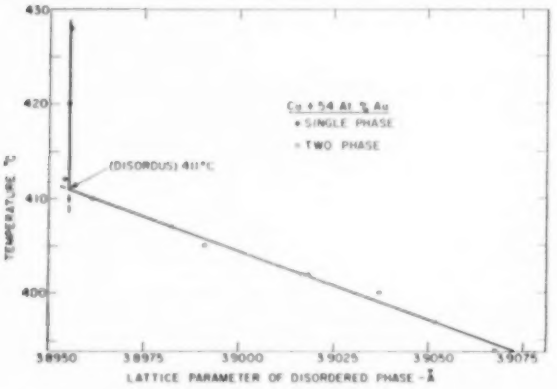


Fig. 1 (above) and 2 (below)—Relation between equilibrating temperature and lattice parameter of the disordered phase for two alloys on opposite sides of CuAu.



the specimen, by means of a small thermocouple probe which was introduced through a hole in the front of the furnace. By making tests with alloys having transformations at known temperatures (Cu_3Au, CuAu) it was found that the presence of the wire specimen does not significantly affect the measured temperature gradient if the wire is less than 0.020 in. in diameter.

The value of the thermal gradient method, as applied in these experiments, does not lie in the absolute accuracy with which transformation temperatures can be measured, but rather in the feature of continuous temperature variation along the length of a single specimen. When all sources of error were considered, it was estimated that the temperature of any point along the specimen was known to an accuracy of ±10°C.

After equilibrium was reached, the wire was quenched and the phases present were identified by making room temperature Debye-Scherrer photographs at various points along the length of the wire. The time required to reach equilibrium was estimated on the basis of previous experiments[2,4] in which electrical resistance of Cu-Au wires was measured as a function of time and temperature. In these resistance tests the specimen was held at constant temperature until no change in resistance, measured to a precision of 0.1 pct, was detected. The temperature was then altered slightly and the resistance was again allowed to become constant. Temperature-resistance curves, obtained in ascending steps of temperature, were superimposed upon corresponding curves made in descending steps. At temperatures within the transformation range, a steady state was approached very slowly, frequently requiring several weeks. For the thermal gradient tests the equilibrating time was always in excess of one month. As a further test of equilibrium it became standard practice to seal two wires of the same composition in the same pyrex tube. One wire was in the as-drawn condition and the other had been previously ordered by cooling it slowly through the transformation range. After the wires had been equilibrated in the thermal gradient, they produced identical Debye-Scherrer patterns when photographed at corresponding points along their lengths. Whenever it was known that equilibrium was not reached, Debye-Scherrer lines were diffuse. In such cases longer heat treatment in the same gradient caused the lines to sharpen.

Three compositions were chosen for study: namely 40, 43, and 54 atomic pct Au. Results of incidental tests on two other Cu-Au alloys near CuAu are also given in the final summary of data. The alloys were made by melting electrolytic gold and oxygen-free electrolytic copper under a low pressure of argon in a quartz tube lined with graphite. The ingots were homogenized and worked into wires 0.017 in. in diameter. Chemical analyses, which were conducted by Lucius Pitkin, Inc., gave the results listed in Table I.

For each of the compositions listed in Table I, a 6 in. length of wire, in the as-drawn condition, was sealed in an individual evacuated glass tube and equilibrated in a temperature gradient of about 25°C per cm. The tube was then quenched into water and a stripe of high purity annealed copper powder in an amorphous binder was painted along one side of each wire. In this way, calibration lines of known diffraction angles were recorded on the photographic film along with the Debye-Scherrer pattern produced by the specimen wire. By using these calibration lines, the diffraction angles of the lines from the wire specimen could be measured with good accuracy. The photographs were made with a 10-cm diameter cylindrical camera, which was designed to accommodate the long wire specimen.[3] Copper radiation ($K\alpha_1$ = 1.5405A) was used throughout.

Results: The diffraction patterns made at the high temperature end of all wires were characteristic of a disordered face-centered cubic structure with lattice parameters as listed in Table I. At the low temperature end the patterns were similar to those reported by Johannson and Linde[5] for their CuAu II

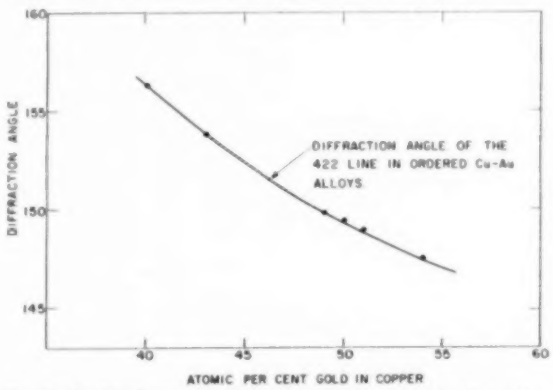


Fig. 3—Empirical curve showing the dependence of the diffraction angle of the 422 Debye-Scherrer line as a function of composition for ordered Cu-Au alloys.

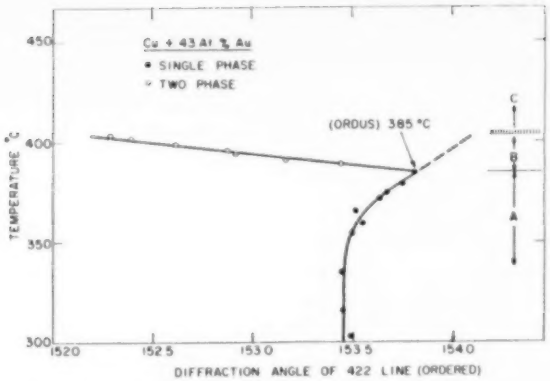
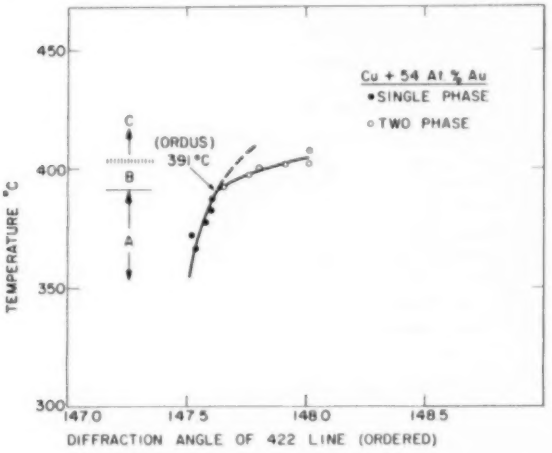


Fig. 4 (above) and 5 (below)—Relation between equilibrating temperature and the diffraction angle of the 422 Debye-Scherrer line of the ordered phase for two alloys on opposite sides of CuAu.



orthorhombic structure. A thorough study of the CuAu II structure was not made. Presumably, if the wires had extended to low enough temperatures and the annealing periods were sufficiently long, the tetragonal CuAu I structure would have been found at the low temperature end.

In each specimen there was a range of temperature over which patterns corresponding to the ordered CuAu II and the disordered structures were found on the same film. It was not assumed that equilibrium was reached unless all the lines of each pattern were sharp and back-reflection doublets were clearly resolved. To give such patterns, each of the diffracting particles must have been uniform in composition, relatively unstrained, and greater than 1000Å in minimum dimension. In the paragraphs that follow, the two patterns are discussed separately in terms of the manner in which they change with annealing temperature.

Disordered Cubic Structure

The lattice parameters corresponding to the disordered structure were calculated for various annealing temperatures. At temperatures where only the disordered pattern was visible on the film, the lattice parameter remained independent of temperature. Where both patterns were present, there was a decided temperature dependence, as shown in Figs. 1 and 2. This behavior can be interpreted in terms of changing composition of the disordered material with temperature, according to conventional tie-line segregation across a two-phase region between the ordered and disordered fields. The two-phase region would be expected to ascend from both sides of the CuAu composition toward a maximum transformation temperature at 50 atomic pct. If this construction is correct, then the lattice parameter of the disordered phase in alloys on the copper-rich side of CuAu should increase with temperature because the disordered phase becomes richer in the component of larger atomic radius, i.e., gold, as the temperature increases. Conversely, in alloys on the gold-rich side of CuAu, the lattice parameter should decrease with increasing temperature because the disordered phase becomes leaner in gold. These effects were observed in all the Cu-Au alloys where a two-phase region was found.

If the data contained in Figs. 1 and 2 are used, the true disordus temperature can be found by extending the sloping lines to the lattice parameter of the alloy when it is all disordered. The intersection marks the disordus temperature for the composition in question. Knowing the dependence of a_o on composition, the portion of the disordus line which is associated with the overall composition of the specimen can be calculated. This is shown in Fig. 6, which is discussed in a later section.

Ordered Structure

The reflection angle of the 422 line in the ordered pattern varies with composition according to the experimentally determined curve in Fig. 3. These data were taken from Debye-Scherrer photographs made at points on the thermal gradient wires that had been equilibrated at least 25°C below the two-phase temperature range.

At temperatures well below those at which the last traces of the disordered pattern were seen, the diffraction angle of the 422 line was independent of temperature. As the two-phase region was approached the reflection shifted gradually to a higher angle. As soon as the two-phase region was entered, however, as indicated by the presence of the two patterns on the film, there was a marked dependence of the diffraction angle upon temperature. For the 43 pct Au alloy the shift was toward a lower angle with increasing temperature, and for the 54 pct alloy, the shift was toward a higher angle. This behavior is summarized in Figs. 4 and 5.

In the temperature range *C*, only the disordered pattern was observed; in range *B* both ordered and disordered patterns were seen, and in range *A* the disordered pattern was entirely replaced by the ordered. The ordus temperature can be located by the intersection of the lines in the *A* and *B* temperature ranges.

Evidently the shift to higher angle, as the two-phase region is approached, is a result of a lowering of the degree of long range order of the ordered

Table I. Chemical Analyses of Alloys

Nominal Composition, Atomic Pct Au	Composition by Analysis		Actual Atomic Pct Au	Disordered Phase a_o, A
	Wt Pct Cu	Wt Pct Au		
40	32.61	67.35	39.97	3.832±0.001
43	29.88	70.08	43.06	3.845±0.001
50	24.39	75.58	49.99	3.876±0.001
51	23.59	76.38	51.16	3.882±0.001
54	21.58	78.40	53.95	3.895±0.001
Cu	Spectroscopically pure			3.615±0.001

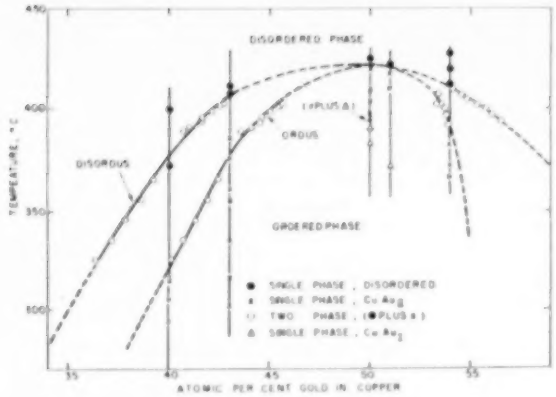


Fig. 6—Part of the Cu-Au equilibrium phase diagram.

phase. Within the two-phase region, the shift must have two components: 1—the effect of the changing composition of the ordered phase by tie-line segregation, and 2—the continuing shift to higher angles due to lowering long range order as the temperature is raised. The two components can be resolved and their magnitude estimated by extrapolating the line in region *A* into region *B*, as shown by the dashed line. The deviation of this line from its position at lower temperatures where θ is constant, represents the component due to the lowering long range order of the ordered phase. The horizontal distance between this extrapolated line and the experimentally determined line in range *B* would then represent the component of angular displacement due to composition change only. The magnitude of this change in composition can be estimated by referring the latter component of angular displacement to the experimentally determined curve of Fig. 3. This interpretation is consistent with a graphical scheme, described in an earlier paper,[8] whereby the degree of long range order of the ordered phase is specified below and within the temperature range where both disordered and ordered phases coexist in equilibrium. It will be noticed that the angular shifts, in the temperature range *B*, are in opposite directions for alloys on opposite sides of the CuAu composition. Also, in each case the direction of the displacement is such that, when referred to Fig. 3, the composition of the ordered phase can be reasonably interpreted in terms of tie-line segregation, that is, the ordus lines slope toward a maximum at 50 atomic pct.

Discussion: The results described above can be summarized by means of the partial Cu-Au equilibrium diagram shown in Fig. 6. This diagram was constructed solely on the basis of the experimental data described above. By measuring the relative intensities of characteristic lines in the ordered and disordered patterns, it should be possible to make an independent determination of the relative amounts of the ordered and disordered phases through the two-phase region. This was not possible in the present study, however, because the necessarily long annealing times produced such large grains that Debye-Scherrer lines were too spotty to be measured accurately with the usual photometric equipment.

The diagram evidently contains two-phase regions which conform to the requirements of the Gibbs phase rule for heterogeneous equilibrium in a binary system. Therefore, in alloys near CuAu, the ordered and disordered states should be treated as different phases.

By 1940, the sort of binary diagram found in this investigation had been proposed by at least four other investigators.[7] Since then, however, due to a growing misconception that order-disorder transformations generally are homogeneous changes of state, the two-phase region separating the order and disorder fields has frequently been replaced by a single dashed line, which is supposed to show the temperature above which no long range order exists.[8] Such a construction is not in accord with the experimental facts described here.

The present study shows a major deviation from the results of early workers who proposed phase diagrams containing an invariant maximum point at 40 atomic pct Au composition. In the present work no indication of congruent transformation was found at this composition. Since the experimental method used here is more direct than the methods used by others, such as measurements of the electrical resistivity or of the specific heat, it is reasonable to conclude that no superlattice exists which has a stoichiometric composition of Cu_3Au_2.

Summary

1—X-ray evidence is given which shows that in Cu-Au alloys near CuAu in composition there is a finite temperature range within which the ordered and disordered states can coexist in equilibrium as conjugate phases. The transformation may therefore be regarded as heterogeneous or first-order.

2—Debye-Scherrer effects are interpreted in terms of normal tie-line segregation across two-phase regions separating the ordered and disordered fields near CuAu in the Cu-Au equilibrium phase diagram.

3—Part of the Cu-Au equilibrium phase diagram is plotted on the basis of observed Debye-Scherrer effects. The horizontal and vertical widths of the two-phase regions are about 3 atomic pct and 20°C, respectively, at both 43 and 54 atomic pct Au. In general, however, the two-phase regions are not symmetrical about the composition CuAu.

4—It is unlikely that an ordered structure exists which has a stoichiometric composition Cu_3Au_2 since the equilibrium transformation at this composition is divariant.

Acknowledgments

The author is indebted to R. A. Oriani, D. Turnbull, and A. H. Geisler for their helpful comments during the writing of this paper.

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Self-Diffusion of Iron in Iron Oxides and The Wagner Theory of Oxidation

by L. Himmel, R. F. Mehl, and C. E. Birchenall

The rates of self-diffusion of iron in artifically prepared wustites of various compositions have been determined using the decrease in surface activity technique. Similar measurements are reported for artificial magnetites of nearly stoichiometric composition and for natural hematite single crystals. These data, together with appropriate thermodynamic data derived from the present study or from the literature, are used to calculate the rates of oxidation of iron and its oxides, taking as a basis the theoretical rate equations developed by Wagner. The calculations are compared with experimental rate constant data for these same reactions and are shown to provide essential confirmation for the Wagner theory. For the most part, the results are also consistent with the previously proposed transport mechanisms in the oxides of iron.

WHEN a metal is exposed to an oxidizing atmosphere at elevated temperatures, a superficial oxide layer is formed which then thickens according to some characteristic rate law. Provided that the oxide layer is dense and continuous and does not present any paths for gaseous diffusion, continued growth must inevitably involve the migration of the reactants—either the metal or oxygen or both—through the lattice of the solid oxide. This is true whether the reaction rate is controlled by the diffusion process itself or by a slow step in a reaction at one of the interfaces. If the overall rate is limited by diffusion, and if the concentrations or thermodynamic activities of the reactants at the boundaries of the oxide layer are independent of time, the familiar parabolic rate law is observed.

Under these conditions, Wagner[1] has shown that the rate constant may be expressed in terms of the mobilities of the reacting components and the appropriate concentration or activity gradients which are established across the growing oxide layer. In presenting the phenomenological basis for the theory, Wagner has emphasized the role played by lattice defects in diffusion processes in oxides. The essential validity of this theory has been confirmed by experiment for a number of simple systems including the growth of Cu_2O on copper.[2-4]

One of the objectives of the present study has been to extend the Wagner approach to the more complex process of the oxidation of iron and its oxides, and particularly to wüstite, which is normally the major constituent of the oxide scales formed on iron at temperatures above approximately 570°C. For this purpose the rates of self-diffusion of iron in wüstite, magnetite, and hematite have been measured by tracer techniques and the necessary thermodynamic data have been obtained from equilibrium studies involving the oxides and their atmospheres. These data have subsequently been used to test the underlying assumptions of the Wagner theory as well as the detailed mechanism of the scaling of iron previously proposed by Davies, Simnad, and Birchenall.[5]

Lengthy treatments of diffusion and conduction phenomena in ionic crystals have been published.[6, 7] The latest, by Jost,[8] also summarizes much of the existing experimental data. In general, however, the oxides of iron have not been considered specifically and hence a brief review of the available

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structural and transport data for these materials will be pertinent.

Crystal Structures of the Oxides of Iron

Since the radius of the oxygen ion is approximately 1.4Å as compared to roughly 0.8Å for Fe^{++} and 0.7Å for Fe^{+++}, it is often convenient to regard all three oxides as relatively close-packed networks of oxygen ions with the smaller iron ions arranged in the interstices. The structures of the oxides of iron and the interrelations between them are discussed in considerable detail by Goldschmidt.[9]

Wüstite: In wüstite the oxygen ions and the cations occupy separate, interpenetrating, face-centered cubic lattices in the NaCl-type structure. This oxide is unstable, in bulk, below approximately 570°C, slowly decomposing into a eutectoid mixture of α-iron and magnetite. It is not observed as a stable constituent of the oxide layer on iron below this temperature.

Magnetite: According to Verwey and coworkers,[10-12] magnetite possesses the cubic, inverse spinel structure in which the oxygen ions have a cubic, close-packed arrangement. Among the sites available to the cations in the ideal unit cell of the spinel structure, eight are tetrahedral positions and sixteen octahedral positions. At the stoichiometric composition, the eight tetrahedral sites are occupied by Fe^{+++} ions, while the distribution of the remaining eight Fe^{+++} and eight Fe^{++} ions about the sixteen octahedral positions is random and fluctuating. This model satisfactorily accounts for the high electrical conductivity of magnetite at ordinary temperatures and may also be used to explain the unique structural transition observed in this oxide at low temperature.[13]

Hematite: Hematite or α-Fe_2O_3 has the corundum structure, the symmetry being rhombohedral. The structure is best viewed as a slightly distorted, hexagonal close-packing of oxygen ions with the metal ions again residing in the interstices. A cubic, ferromagnetic variety of ferric oxide, designated as γ-Fe_2O_3 and having a structure very similar to that of magnetite has also been reported.[14] Apparently this oxide is always metastable with respect to hematite;[15] it is never observed in the oxide scales formed on iron at high temperatures.

Defect Structures and Transport Mechanisms in the Oxides of Iron

Diffusion and the related phenomenon of conductivity in oxides (and sulphides, halides, etc.) are commonly associated with the migration of ions and electrons rather than electrically neutral atoms or molecules. Although the cations, anions, and electrons all have some mobility in these materials, the transference number of one of the component particles generally far exceeds that of the others. Such marked differences in the mobilities of the various species can frequently be understood by a consideration of the structure of the crystal and the type of lattice defects which are present. In most oxides, for example, ionic transport can be attributed almost entirely to the metallic ions, either through the migration of cation vacancies as in Cu_2O, NiO, etc., or of interstitial ions as in ZnO, etc. In the alkali halides, where defects occur in both the cation and anion sites, the cations are often substantially more mobile because of their smaller size. Only a few examples are known in which the transport is due predominately to the migration of negatively charged anions or anion vacancies.[1, 9]

Wüstite: As shown by several investigators, notably Darken and Gurry,[16] wüstite exists as a thermodynamically stable, single-phase structure over a relatively wide range of compositions, that does not seem to include the stoichiometric compound FeO. The maximum iron content found by Darken and Gurry corresponds to $Fe_{0.948}O$ and by Jette and Foote[17] to $Fe_{0.953}O$. Recent claims by Benard[18] that the stoichiometric compound is stable at temperatures above approximately 800°C have not been adequately substantiated.

Wüstite, like Cu_2O and NiO, is a cation-deficient structure. Jette and Foote have demonstrated by a comparison of X-ray lattice parameter and density measurements that an appreciable fraction of the lattice sites normally occupied by iron ions are vacant. Since the oxygen lattice is thought to be perfect, two Fe^{++} ions must be promoted to the ferric state for each vacant iron site, in order to maintain electrical neutrality. A recent correlation of the existing thermodynamic data for ferrous oxide by Kelley[19] indicates that the vacancies themselves may be ordered instead of randomly distributed, as had previously been assumed.

Agreement on the transport mechanism in wüstite has been fairly universal since the work of Jette and Foote. The belief that ionic transport in wüstite occurs essentially by the interchange of vacancies with normal lattice sites is strongly supported by the observations of Wagner and Koch[20] on the electrical conductivity of wüstite as a function of oxygen pressure, and by marker movement studies of Davies, Simnad, and Birchenall.[5] Wagner and Koch found, in fact, that the electrical conductivity of wüstite between 800° and 1000°C is roughly proportional to the 8th root of the oxygen pressure. Nevertheless, the early but rather crude marker experiments of Pfeil[21] could have been interpreted to allow for considerable oxygen ion diffusion, while the more recent work of Dunnington, Beck, and Fontana[22] places this contribution at approximately 10 pct.

Magnetite: Considerable disagreement exists in the literature regarding the stable range of the magnetite phase field. The most reliable evidence indicates that the deviations from stoichiometric ratio are in the direction of increased oxygen content. The homogeneity range is much narrower than that for wüstite, yet still of detectable magnitude. Verwey and Haayman[11] have shown by X-ray lattice parameter measurements that the deviations from stoichiometric composition are actually associated with the presence of vacancies in the cation sites rather than excess oxygen in interstitial positions. Defects are assumed to occur only in the octahedral sites, the Fe^{++} ions being replaced by Fe^{+++} and vacancies. It is also assumed that the vacant positions are statistically distributed over the available octahedral sites.

Although it would seem that the structure of magnetite is well established, studies of transport phenomena in this oxide appear to be contradictory. Thus Wagner and Koch found the electrical conductivity of magnetite to be essentially independent of the oxygen pressure. Furthermore, the marker movement experiments of Davies, Simnad, and Birchenall indicate a ratio of oxide ion mobility to iron ion mobility of almost four to one* in the

* It now appears that this conclusion is in error. A brief note correcting the original interpretation of the marker experiments will be published by Davies, Simnad, and Birchenall.

neighborhood of 900°C. The latter result, particularly, is difficult to reconcile with the structural model given by Verwey.

Hematite: The departure from stoichiometric composition in α-Fe_2O_3 is practically undetectable by analytical methods. Nevertheless, since the ferrous and ferric states of oxidation are the only ones readily available to iron, it would be expected that hematite is slightly oxygen deficient. Such a deficiency can be accounted for in either of two ways; i.e., the presence of oxide ion vacancies or interstitial iron ions. The existing information does not permit a clear-cut distinction between these two possibilities, although the former appears more likely.

Wagner and Koch were not able to observe any effect of oxygen pressure on the conductivity of α-Fe_2O_3, but Bevan, Shelton, and Anderson[23] have concluded, from similar studies, that conduction in this material most probably occurs by an oxide ion vacancy mechanism. Pryor and Evans[24] have employed the anion vacancy model to explain the dissolution behavior of hematite in acids. The interpretation of marker movement studies of Davies, Simnad, and Birchenall is somewhat uncertain but is also consistent with the vacancy picture. It should be pointed out, however, that the effect of oxygen pressure on the concentration of oxide ion vacancies cannot be distinguished from its effect on interstitial iron ions; the number of either kind of imperfection is decreased by an increase in oxygen pressure.

Self-diffusion data for iron in sintered hematite powder compacts have recently been reported by Lindner.[25] The significance of these measurements will be discussed in connection with the results obtained in the present investigation.

Experimental

The decrease in surface activity technique has been selected for the self-diffusion experiments. This choice was dictated largely by a consideration of the physical and chemical properties of the oxides themselves. Although preference is normally given to a sectioning method, the removal of uniformly thin layers of the bulk oxides for radiochemical analysis became prohibitively difficult. All of the wüstites and magnetites used in this work have been prepared by the direct oxidation of high-purity iron. Each specimen has been oxidized to completion at high temperature and then homogenized for prolonged periods in atmospheres of constant, known oxidizing potential. Not only did this technique permit close control over the composition and purity of the resulting oxides, but it invariably yielded dense products which were essentially free from cracks, voids, or other structural irregularities. Surprisingly enough, the hematites obtained in this manner were always rather porous and had very little mechanical stability. Natural single crystals of this oxide were employed instead of the artificially prepared material for this reason.

Materials: High-purity iron supplied by the National Research Corp. has been used as the starting material for the preparation of the oxides. This iron was received in the form of a 3-in. diam vacuum-melted and cast ingot. Insofar as chemical purity is concerned, it is very similar to the Westinghouse "Puron" employed in the kinetic studies of Davies, Simnad, and Birchenall. The maximum impurity contents, based on spectroscopic standards, are as follows: 0.02 pct O, 0.001 pct N, 0.005 pct H, 0.005 pct C, and 0.02 pct total metallic impurities. No attempt has been made to refine or further purify the as-received material.

The specimens were cut from blanks machined from the original ingot. They were in the form of disks approximately 2 cm in diameter and 1.5 to 2.5 mm thick, the thickness depending upon the temperature at which homogenization was to be effected. Each specimen contained a lip, integral with the disk, through which a small hole was drilled to facilitate suspension of the sample in the oxidation unit. After cutting to approximate shape and dimensions, both faces of the specimens were surface ground; the edges were also smoothed to reduce the tendency for subsequent cracking and spalling of the oxide layer.

Several large, natural, hematite crystals (α-Fe_2O_3) from Minas Geraes, Brazil, were obtained. The useful single crystals were selected primarily on the basis of their freedom from associated minerals or other structural faults. Even when finely pulverized, however, they were too slowly attacked by strong acids to obtain satisfactory analytical samples. Nearly all of the crystals selected possessed highly reflecting and remarkably well-developed crystal faces. The orientations of the most prominent faces of each crystal were determined by the back-reflection Laue technique. In general, these faces corresponded to the (00.1) or basal planes of the crystal. Rectangular parallelepipeds approximately $\frac{3}{4} \times \frac{1}{2} \times \frac{1}{4}$ in. were cut from the larger crystals using a water-cooled diamond cut-off wheel, the sectioning being accomplished so that the largest face of each crystal either contained or was perpendicular to the basal plane of the rhombohedral crystal.

The radioactive iron was obtained as an aqueous chloride solution from the Isotopes Div. of the United States Atomic Energy Commission. When originally received, this solution contained both Fe^{55} and Fe^{59} in roughly equivalent concentrations. The desired isotope is Fe^{55} which decays by K-electron capture with the emission of soft X-rays (Mn K, λ = 2.10A). Since Fe^{55} has a half-life of approximately 2.9 years as compared to roughly 46 days for Fe^{59}, the radioactive unit was allowed to decay for a period of more than a year before use in order to decrease the Fe^{59} concentration to well below 0.5 pct. The active unit was then twice purified by continuous ether extraction from hydrochloric acid solution, after which the ether extract was evaporated to dryness and made up to the desired specific activity with distilled water. Absorption and decay measurements on samples taken from the ether extract served to establish its radiochemical purity.

Description of the Oxidation System: The wüstites were prepared and diffused in hydrogen-water vapor atmospheres in a dynamic system designed specifically to provide accurate control over the oxidizing potential of the furnace gases. This system consisted essentially of a fairly elaborate gas purification train, a saturator maintained at known constant temperatures for introducing controlled amounts of water vapor into the gases, and an electrically heated reaction chamber in which the specimens were suspended. The apparatus was of all-glass or silica construction and was operated under a slight positive pressure of 10 mm Hg. Hydrogen-water vapor mixtures generated in the saturator were preheated to the furnace temperature and then passed through the reactor at a vigorous rate to minimize the tendency for thermal segrega-

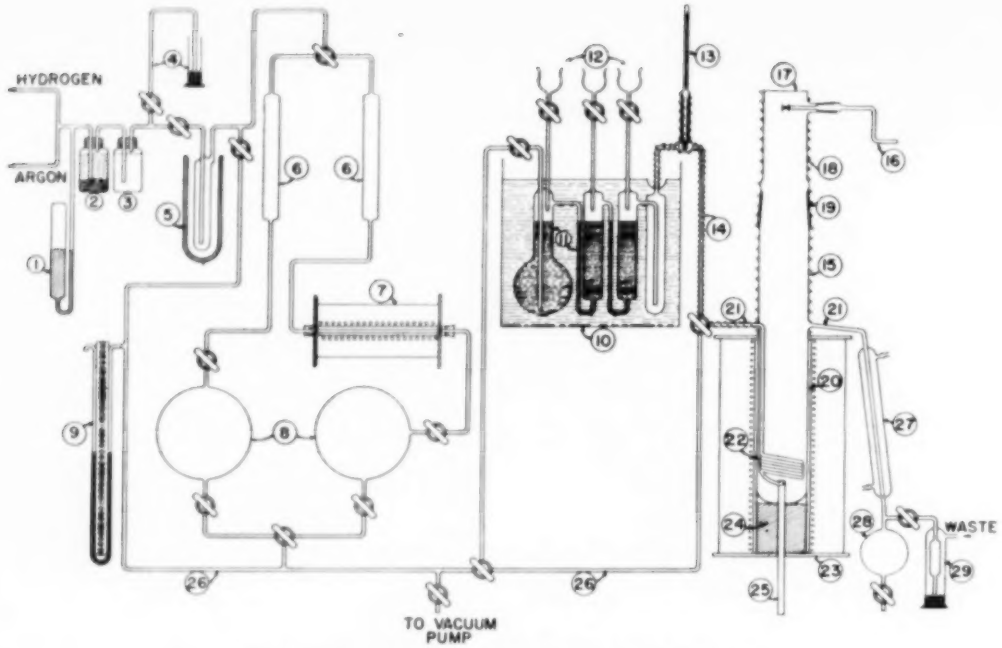


Fig. 1—Schematic diagram of the oxidation and diffusion unit.

1—Safety trap.
2—Vanadyl sulphate + Zn amalgam.
3—Gas scrubbing tower.
4—Vent line.
5—Cold trap.
6—Auxiliary drying towers.
7—Furnace containing Ti chips.
8—Vacuum-flask storage reservoirs.
9—Mercury manometer.
10—Constant-temperature oil bath.
11—Saturator.
12—Funnel tubes.
13—Mercury thermometer.
14—Electrically heated line.
15—Nichrome heating element.
16—Winch.
17—Optical window.
18—Glass head.
19—Ground joint.
20—Fused silica reaction chamber.
21—Graded silica-to-pyrex seals.
22—Silica preheating spiral.
23—Kanthal-wound resistance furnace.
24—Alundum support.
25—Silica thermocouple well.
26—Bypass line.
27—Water-jacketed condenser.
28—Collecting flask.
29—Constant-head trap.

tion in the gas phase. The gases were not analyzed directly. Instead, the ratio P_{H_2O}/P_{H_2} of the atmosphere in the reaction chamber was calculated from the partial pressure of water vapor at the temperature of the saturator and the total pressure in the system. The apparatus is shown schematically in Fig. 1.

Gas Purification System: Commercial hydrogen or argon was led through the safety trap (*1*) into the scrubbing unit (*2*), (*3*) where traces of oxygen in the gas stream were removed. This unit contained 0.1 M vanadyl sulphate solution together with lightly amalgamated 20 to 30 mesh zinc powder; the principle of operation has been described by Meites and Meites.[8] Water vapor was effectively removed by condensation in the cold trap (*5*) and by absorption in the auxiliary drying towers (*6*) which were filled with "Ascarite" and activated alumina. The argon was further purified by allowing the gas to flow over titanium chips maintained at a temperature of 1000°C in a small resistance furnace (*7*). Vacuum-flask storage reservoirs (*8*) were provided for each of the pure gases. These reservoirs were by-passed (*26*) during the greater part of each run; they were useful, however, for rapid refilling of the system after it had been evacuated. The two reservoirs were joined through a three-way stopcock to a common line leading to the saturator.

The Saturator: This unit (*11*) comprised a presaturator flask, two saturating towers, and a mixing chamber joined together in that order. The first three sections were partially filled with water while the mixing chamber was left empty. The overall capacity of the saturator was approximately 500 cc. Fritted glass disks were sealed into the base of the second and third towers to disperse the gases and insure complete saturating efficiency. Funnel tubes (*12*) with stopcocks attached permitted the individual compartments of the saturator to be refilled, during a run if necessary, without introducing air into the system. The entire unit was completely immersed in a well-insulated oil bath (*10*) whose temperature was maintained constant to within ±0.01°C by means of a mercury-toluene thermoregulator in conjunction with a sensitive thyratron tube relay circuit. A clear, low-viscosity mineral oil was used as the bath medium to allow continuous observation of the water level in the saturator. Temperatures were read on a mercury-in-glass thermometer with 0.1°C subdivisions which had been calibrated against a National Bureau of Standards thermometer. A Beckmann differential thermometer was also employed to indicate the normal temperature fluctuations in the bath.

The saturator was joined to the reaction chamber through an electrically heated line (*14*) which was kept at a temperature of roughly 10° to 15°C above that of the saturator in order to prevent condensation. The temperature was indicated on a mercury thermometer (*13*) with a standard taper joint inserted in a side-arm tube attached to the heated line. A bypass (*26*) was also provided so that hy-

drogen or argon could be admitted to the reaction chamber directly from the gas purification system.

Reaction Chamber: The reactor (*20*) was a gas-tight 22-in. long, 1¾-in. diam fused silica tube fitted with a removable glass head (*18*), a silica preheater spiral (*22*), and a thermocouple well (*25*). It was mounted vertically with the lower half of the silica tube surrounded by a heavy Kanthal-wound resistance furnace (*23*). The protruding upper section was wrapped externally with nichrome wire (*15*) and suitably lagged with asbestos; this winding was actually continuous with that of the heated line from the saturator.

The glass head incorporated a winch (*16*) for manipulating and positioning the specimens in the reaction tube, and an optical window (*17*) through which the samples could be observed. By means of this arrangement, the specimens attached to the winch could be raised or lowered without reopening the system. Another highly important requirement was also fulfilled, namely, that the gas composition could be adjusted and the temperature stabilized before the specimens were introduced into the hot zone of the furnace. The removable head was connected to the silica tube through a standard taper ground joint which was sealed with Picein or Apiezon cement after the specimens had been inserted. This part of the system was also heated to prevent condensation.

The gas preheater (*22*) consisted of approximately six turns of 3/16-in. diam silica tubing wound into the form of a helix, having an inside diameter of roughly 1¼ in. It was supported concentrically inside the lower end of the chamber and joined to the heated line from the saturator through a graded silica-to-pyrex seal (*21*). The gases from the saturator passed downward through the preheater coil and entered the reaction chamber at a point very close to the thermal center of the furnace. Since the gas flow in the chamber was directed upward, and the specimens were suspended immediately above the gas inlet tube, the samples were continually bathed by fresh gases from the saturator. The linear flow rate of the gases in the reaction zone was of the order of 1 cm per sec at furnace temperature.

The gas-tight silica thermocouple well (*25*) was sealed into the bottom or closed end of the reaction chamber in such a way that the temperature of the entering gases could be determined. A Pt-Pt-Rh thermocouple calibrated against a secondary standard was employed for this purpose. The actual specimen temperature was measured both before and after each run by inserting another calibrated Pt-Pt-Rh thermocouple through the top of the reaction tube to the exact level at which the specimens were suspended. Temperatures determined in this fashion rarely differed from the inlet gas temperature by more than 1° or 2°C.

Except for a few minor details, the furnace design was fairly conventional. The Kanthal heating element was gradient wound on an alundum core into which the reaction chamber fitted rather snugly. A zone roughly 3 in. long was obtained within which the temperature did not vary by more than ±1°C. The reaction tube was so positioned in the furnace by an alundum support (*24*) that the location of the constant-temperature zone and that of the preheater spiral practically coincided. It was precisely in this region that the specimens were suspended. Furnace temperatures were controlled to within ±1°C by a Leeds and Northrup Micromax recorder.

The gases which passed through the reaction chamber discharged into a water-jacketed condenser (*27*) where the residual water vapor was removed and collected in a receiving flask (*28*). From here the gases bubbled through a constant-head mercury trap (*29*) before being sent to waste.

An apparatus essentially similar to the one just described, but of much simpler construction, was used for the preparation of the magnetites. In this case, oxidation was performed in a flowing water vapor atmosphere using argon as the carrier gas.

Oxidation and Homogenization Procedure: Iron specimens of the approximate thickness employed here could be completely converted to the oxide in a relatively few hours at about 1000°C, provided the atmosphere was sufficiently oxidizing to maintain a large concentration gradient across the scale layer. In atmospheres of lower oxidizing potential, where the concentration gradients are shallow, and at lower temperatures where the diffusion rates are slower, the oxidation times may be of the order of several days. Since a long homogenization period is also required, every effort was made to reduce the oxidation times. Therefore, all specimens, regardless of subsequent homogenization treatment, were oxidized completely to wüstite in atmospheres of high oxidizing potential at temperatures of approximately 985°C.

The original iron specimens were polished through No. 3/0 emery paper, carefully degreased in benzene and in alcohol, and then weighed to within ±0.1 mg on an analytical balance. They were then fastened to a silica hook with a heavy platinum wire and the hook in turn was suspended from the winch by a fully annealed 33-gage platinum wire. An alundum sleeve threaded through the hole in the lip of each specimen prevented direct contact between the platinum and the iron. Contamination by slow reaction with the alundum sleeve was confined to the lip of the specimen; this lip was removed following the oxidation and homogenization period. Two specimens were oxidized simultaneously in each run. The oxidation times varied between 14 and 18 hr depending upon the sample thickness, the product being an inhomogeneous wüstite of average composition either higher or lower than that desired.

Homogenization was effected without removing the specimens from the reaction zone. It was simply necessary to readjust the saturator temperature to obtain the appropriate water vapor to hydrogen ratio and then lower the furnace temperature. Four different homogenization temperatures were employed: 983°, 897°, 800°, and 699°C. By systematically varying the ratio P_{H_2O}/P_{H_2} in the gas phase, and allowing sufficient time for equilibrium to be established in each case, a series of homogeneous wüstites covering the range of stability of this oxide were prepared at each of the first three temperatures.

In order to obtain an indication of the times required at each temperature, a series of step-wise homogenization experiments were performed in which samples were weighed at intervals until a constant weight was recorded. The progress of homogenization of one such sample at 983°C is shown in Fig. 2. Unfortunately, the thermal cycling to which the specimens were subjected eventually caused cracking and spalling of the oxides; hence, this technique had to be abandoned when the diffusion specimens were prepared. Based on these control runs, however, the homogenization times could

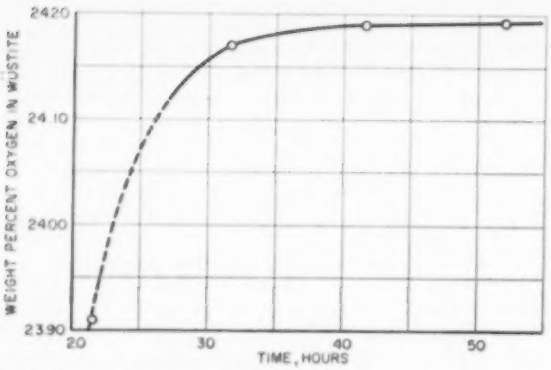


Fig. 2—Progress of homogenization of a wustite specimen in a 20 pct H_2-80 pct H_2O atmosphere at 983°C.

be estimated fairly accurately. The actual times employed ranged from 45 to 109 hr at 983°C, from 73 to more than 150 hr at 897°C, from 150 to 250 hr at 800°C, and were in excess of 300 hr at 699°C. The longer times at each temperature corresponded to the oxides of lower oxygen content since the diffusion rates in these oxides were somewhat slower.

In a further effort to achieve complete homogeneity, two-stage homogenization treatments were introduced at the lowest temperatures. The specimens were first annealed at 983°C and then subjected to a much lengthier homogenizing treatment at 800° or 699°C. The gas composition was adjusted in each part of the cycle so as to obtain an oxide of the same predetermined composition. These operations again were performed consecutively without an intervening quench to room temperature.

After the oxidation cycle was completed, the system was quickly evacuated and filled with pure dry argon. The specimens were then raised to the cold end of the reaction chamber and allowed to cool essentially to room temperature in argon, in order to prevent any change in surface composition. When cool, the specimens were reweighed and the average oxide composition was then calculated from the weight gain. One of the completed wüstite specimens is illustrated in Fig. 3a; the same specimen after diffusion is shown in Fig. 3b.

It was found by microscopic examination that the gas quench was always sufficiently rapid to suppress completely the decomposition of the wüstite eutectoid. However, proeutectoid precipitation of magnetite was observed, and, in fact, could not be avoided, in the oxygen-rich wüstites. A rather extreme example of this type of precipitation is shown in Fig. 4. Faster quenching rates, such as would have been obtained, say, by dropping the oxides into mercury, could not be employed because of the danger of shattering the specimens. Gas-quenching in argon was about equivalent to an air cool and represented a compromise between the degree of precipitation on the one hand, and the tendency for cracking on the other. The effect of such precipitation on the magnitude of the observed self-diffusion coefficient in wüstite is discussed in more detail below.

The magnetites were prepared in essentially the same manner. Oxidizing temperatures varied between about 980° and 990°C while the time for complete conversion to magnetite in a flowing argon-water vapor atmosphere was approximately 150 hr at these temperatures. An additional 150 hr or so was allowed for homogenization, after which the specimens were again gas-quenched in argon. A deliberate attempt to vary the composition of the resulting oxides was not made because the extent of the magnetite phase field is very limited at temperatures below 1000°C.

Diffusion Technique: The standard procedure adopted for the diffusion runs was as follows: A flat surface was prepared on each specimen upon which a thin film of radioactive iron (Fe^{55}) was deposited by plating from aqueous solution. After counting to determine the initial surface activity, each specimen was diffused in its own equilibrium atmosphere so as to prevent any change in composition during the diffusion anneal. The specimen was then recounted to establish the fraction of the original surface activity remaining after diffusion. From this activity ratio and the previously determined absorption characteristics of the oxide, the self-diffusion coefficient was calculated.

Inasmuch as the raw oxides had rather rough surfaces (see Fig. 3), one face of each specimen was

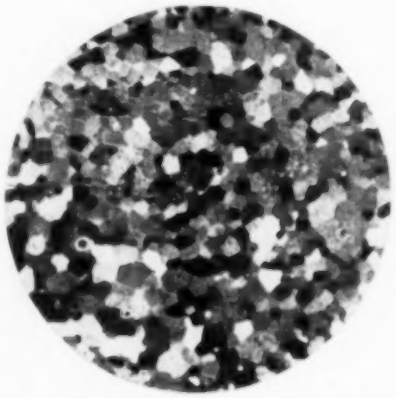


Fig. 3—General appearance of wustite disks prepared by the direct oxidation of iron in hydrogen-water vapor atmospheres.
a (left)—Raw oxide with lip partially intact.
b (above)—Same specimen, with lip removed, after diffusion for 1 hr at 983°C. X3.

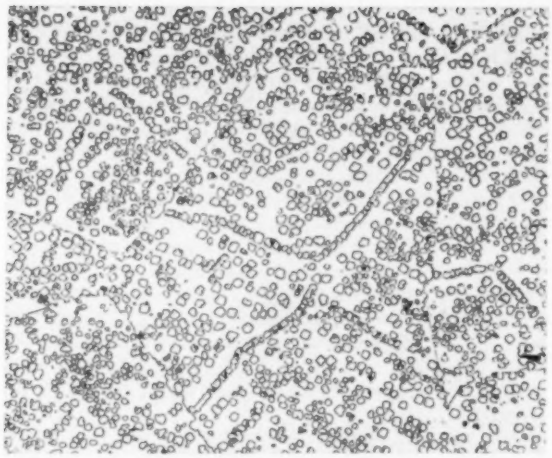


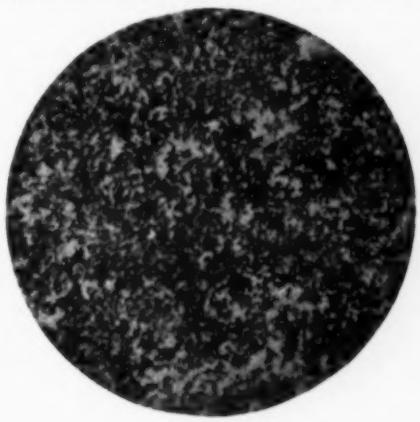
Fig. 4—Proeutectoid precipitation of magnetite from wustite having an average composition of 75.8 pct Fe. Specimen gas quenched in argon from 983°C. Etched in warm dilute HCl. X250. Area reduced approximately 75 pct for reproduction.

ground flat and then given a fine metallographic polish until the surface acquired a brilliant, almost metallic luster. This surface was freed from traces of polishing abrasive, degreased, and then electroplated with radioactive iron using a wet filter paper technique similar to that described by Birchenall and Mehl.[27] The aqueous ferric chloride plating solution contained approximately 4 mg of iron per ml. Roughly 2 to 3 min at a current density of 0.1 amp per sq cm were required to reach the desired activity. The uniformity of plating is indicated by the autoradiograph, Fig. 5a. Since the edges of the specimens were often somewhat porous, the activity was removed from these areas by swabbing with dilute HCl in alcohol and finally the entire specimen was cleaned in alcohol. Enough activity remained in the central area of about 1 sq cm to give a counting rate of between 8,000 and 12,000 counts per min. From the specific activity of the plating solution, the average thickness of the Fe^{55} film was calculated to be between 10^{-5} and 10^{-4} cm.

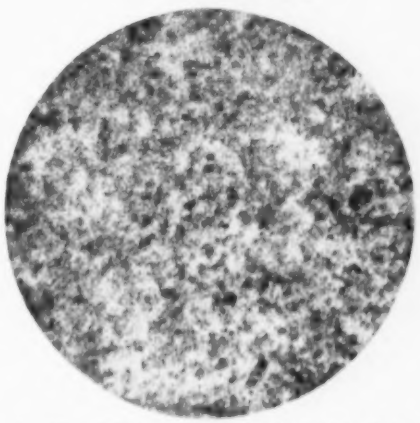
Counting was performed with a Tracerlab "Autoscaler" using a mica end-window, X-ray sensitive Geiger-Müller tube. A total of 40,000 counts was taken on each specimen to reduce the statistical counting error to well below 1 pct. All counts were compared with an internal standard to eliminate normal day-to-day variations in counting efficiency and the usual corrections were made for background and coincidence errors. An individual wax mold, set in a metal cup, was prepared for each sample so that its counting geometry could be accurately reproduced after diffusion.

The diffusion anneal was rather critical, especially for the wüstites, since a change in the composition of the oxide could not be tolerated. For this reason, each wüstite specimen was diffused in the same atmosphere with which it was originally in equilibrium before being quenched from the homogenizing temperature. The specimens were hung in the cold portion of the system until the equilibrium conditions of temperature and atmosphere were established in the reaction tube. After flushing the system for at least 2 hr with the equilibrium gas mixture, the specimen was rapidly lowered into the constant temperature zone. The start of the run was taken as the time at which the specimen became indistinguishable from its surroundings when viewed through the optical window. On the average, a total of about 90 sec was required for the specimen to reach the furnace temperature. The diffusion times for the wüstites were of the order of 1 to 2 hr depending upon the temperature. Longer times could not be employed because the radioactivity level then became too weak for practical use (see Fig. 5b); consequently, rapid heating and cooling were essential. At the end of the predetermined diffusion period, the specimen was quickly raised to the cold part of the system, which was then evacuated and filled with pure dry argon. With these precautions, it is doubtful if the errors introduced by the uncertainty in time measurement exceeded 1 or 2 pct.

Another method of specimen support was required, since the lip by which the sample was suspended during the oxidation and homogenization period had been removed. Each wüstite disk was placed active face up in a perforated platinum pan and covered with a platinum lid. The perforations allowed ready access to the atmosphere. Since the rough, under surface of the specimen made only point contact with the supporting pan, contamination by reaction with the platinum was probably very slight. The platinum lid was frequently checked for activity but no evidence of vaporization losses was ever detected, nor was any significant activity level found in the water condensed from the furnace



a—Before diffusion.



b—After diffusion for 1 hr at 897°C. Note that the original distribution of activity is not altered appreciably by lateral or surface diffusion. X4.

Fig. 5—Autoradiographs of the active or plated surface.

Table I. Calculated Linear Absorption Coefficients for Mn Kα Radiation (λ = 2.103A) in the Oxides of Iron

Oxide	Wt Pct Fe	Density, G per Cu Cm	μ/ρ, Sq Cm per G	μ, Cm^{-1}
Wüstite	75.60	5.56	76.5_7	$425._7$
	75.70	5.57	76.6_0	$426._6$
	75.80	5.58	76.6_8	$427._0$
	75.90	5.59	76.7_5	$429._0$
	76.00	5.60	76.8_1	$430._1$
	76.10	5.61	76.8_7	$431._2$
	76.20	5.62	76.9_3	$432._8$
	76.30	5.63	76.9_9	$433._4$
	76.40	5.64	77.0_5	$434._5$
	76.50	5.65	77.1_1	$435._6$
Magnetite	72.28	5.18	74.6_3	387
Hematite	69.94	5.26	73.2_6	385

gases. Furthermore, the walls of the reaction chamber remained inactive even after more than forty diffusion runs had been performed in the system.

The magnetites were diffused in much the same manner, for times of a few hours to several weeks at temperatures of 987° to 799°C, respectively. In each case the atmosphere contained approximately 90 pct water vapor and 10 pct argon by volume. A pair of hematite crystals of different orientation were diffused simultaneously. These were placed in an alundum boat with their active faces almost in contact to reduce the possibility of vaporization losses. The anneals were performed under essentially static conditions in a horizontal Globar-heated furnace at a pressure of 1 atm of oxygen.

Calculation of the Self-Diffusion Coefficient: Under the conditions of these experiments, the appropriate solution to the diffusion equation is that given by Steigman, Shockley, and Nix.[28] This solution has the form

$$F = e^z \left[1 - \phi(\sqrt{Z})\right] \qquad [1]$$

where F is the fraction of the initial surface activity remaining after diffusion, $\phi(\sqrt{Z})$ is the Gaussian error integral, and Z is a parameter defined by

$$Z = \mu^2 Dt \qquad [2]$$

μ being the linear absorption coefficient, cm^{-1}, D the self-diffusion coefficient, sq cm per sec, and t, the time in seconds. Only the calculation of the absorption coefficient requires further comment.

The absorption properties for the radiation emitted by Fe^{55} were determined with aluminum, copper, and nickel absorbers. It was found that the measured absorption coefficients agreed within a few percent of the known X-ray mass absorption coefficients of these elements for Mn Kα radiation (λ = 2.103A). The agreement was sufficiently good to justify the use of the X-ray values for iron and oxygen, namely 90.9 and 32.2 sq cm per g, respectively. Thus, for a homogeneous iron oxide, the linear absorption coefficient for Mn Kα radiation is given by

$$\mu = \rho\,(90.9\, f_{Fe} + 32.2\, f_O) \qquad [3]$$

where ρ is the density of the oxide, and f_{Fe} and f_O are the weight fractions of iron and oxygen respectively. Wüstite densities were taken from the work of Jette and Foote,[19] the density of magnetite from Smiltens,[20] and that of hematite from Palache, Berman, and Frondel.[30] The values of μ calculated from Eq. 3 are recorded in Table I.

Results

The details of preparation of the lower oxides, wüstite and magnetite, are given in Table II. Only the oxidation and homogenization schedules which yielded massive oxides having the requisite density, purity, and chemical composition are recorded. The resulting oxides were always coarsely polycrystalline with a well-developed columnar grain structure. For the most part, the columnar grains appeared to be oriented so that the axis of preferred growth — very probably the (001) cube direction — was normal to the flat surface of the oxide disk. Although the homogenization times and temperatures varied widely, the average grain diameter was generally between 1 and 2 mm for the wüstites (see Fig. 3b) and of the order of 0.2 to 0.5 mm for the

Table II. Oxidation and Homogenization Treatments for Artificially Prepared Wustites and Magnetites

Specimen No.	Oxidation Treatment: Temperature, °C	Oxidation Treatment: Time, Hr	Oxidation Treatment: Atmosphere, Vol Pct H_2O	Homogenization Treatment: Temperature, °C	Homogenization Treatment: Time, Hr	Homogenization Treatment: Atmosphere, Vol Pct H_2O	Final Composition, Wt Pct Fe
23,24	983	16*	85.0	983	45	85.0	75.65
25,26	981	18*	87.5	983	47	87.5	75.61
27,28	983	18*	80.6	983	52	80.6	75.81
29,30	982	16	84.7	983	48	79.5	75.91
31,32	983	16	84.4	983	60	75.4	76.11
35,36	983	17	82.3	983	84	69.6	76.20
37,38	982	18*	82.6	983	49	82.6	75.76
39,40	983	16*	87.2	983	49	87.2	75.63
41,42	983	17	81.9	983	109	60.2	76.45
43-47	984	150*	90†	984	191	90†	72.31
48-52	985	150*	90†	985	191	90†	72.26
53,54	983	16	84.0	983	73	75.7	76.07
55,56	983	17*	82.5	897	70	82.5	75.65
57,58	983	18	82.1	897	81	74.8	75.97
59,60	983	18	81.8	897	90	67.0	76.14
61,62	983	18	81.7	897	102	58.6	76.35
63,64	983	19	80.4	897	120	50.4	76.55
65,66	983	15	84.7	983	48	82.2	75.80
				800	116	71.3	
67,68	984	15	84.3	983	53	77.3	76.00
				800	130	61.8	
69,70	983	15	85.0	983	58	65.8	76.34
				800	147	50.2	
71,72	981	15	84.6	983	62	58.0	76.73
				800	163	40.7	
73,74	983	14	84.4	983	50	87.5	76.02
				699	241	55.2	
75,76	983	18	84.8	897	100	82.5	75.59
77,78	983	17	84.7	983	103	58.9	76.53
79,80	983	16	84.5	983	62	58.1	76.61
				897	90	49.8	

* Estimated from the results of preliminary experiments.
† Argon-water vapor atmosphere. All other runs performed in hydrogen-water vapor atmospheres.

Table III. Self-Diffusion of Iron in Wustite

Specimen No.	Number of Vacant Iron Sites per Cu Cm x 10^{-21}	Diffusion Treatment		Corrected Surface Activity Ratio, After/Before	Linear Absorption Coefficient, μ, Cm^{-1}	Diffusion Coefficient, D°, Sq Cm per Sec x 10^{-8}
		Time, Sec	Atmosphere, Vol Pct H_2O			
Temperature, 983°C						
25	5.75	3600	87.5	0.0724	426	9.2
26	5.75	3600	87.5	0.0682	426	9.9
39	5.69	3600	87.2	0.0753	426	8.5
23	5.65	3600	85.0	0.0699	426	9.6
24	5.65	3600	85.0	0.0730	426	9.0
37	5.36	3600	82.6	0.0772	427	8.0
38	5.36	3600	82.6	0.0734	427	8.9
27	5.24	3600	80.6	0.0903	428	5.8
28	5.24	3600	80.6	0.0732	428	9.0
29	4.97	3600	79.5	0.0780	429	7.8
53	4.55	3600	75.7	0.0839	431	6.7
54	4.55	3600	75.7	0.0791	431	7.5
31	4.45	3600	75.4	0.0692	431	9.8
32	4.45	3600	75.4	0.0733	431	8.8
35	4.21	3600	69.6	0.0835	432	6.7
36	4.21	3600	69.6	0.0884	432	6.3
41	3.54	3600	60.2	0.1156	435	3.4
42	3.54	3600	60.2	0.1006	435	4.5
77	3.33	3600	58.9	0.1048	436	4.2
78	3.33	3600	58.9	0.0941	436	5.1
Temperature, 897°C						
75	5.80	3600	82.5	0.0989	425	4.9
76	5.80	3600	82.5	0.1079	425	4.0
55	5.65	3600	82.5	0.1325	426	2.7
56	5.66	5400	82.5	0.1112	426	2.5
57	4.81	3600	74.8	0.1102	430	3.8
58	4.81	5400	74.8	0.0928	430	3.6
59	4.37	3600	67.0	0.1163	432	3.4
60	4.37	3600	67.0	0.1198	432	3.3
61	3.81	4500	58.6	0.1217	434	2.5
62	3.81	4500	58.6	0.1290	434	2.2
63	3.27	4500	50.4	0.1213	436	2.4
79	3.11	3600	49.0	0.1259	436	2.8
Temperature, 860°C						
65	5.26	3600	71.3	0.2022	428	1.05
66	5.26	3600	71.3	0.2068	428	1.0
67	4.73	3600	61.8	0.2019	430	1.0
69	3.84	5400	50.2	0.1771	434	0.91
70	3.84	6300	50.2	0.1724	434	0.83
71	2.78	6300	40.7	0.1709	438	0.82
72	2.78	7200	40.7	0.1619	438	0.77
Temperature, 699°C						
73	4.68	3600	55.2	0.3660	430	0.24
74	4.68	7200	55.2	0.2666	430	0.27

magnetites, as determined on the polished diffusion surface.

It has been verified by microscopic examination that all of the specimens listed in Table II were originally single-phase oxides before quenching from the homogenizing temperature. However, proeutectoid precipitation of magnetite was not completely avoided during the quench, except in the wüstites containing greater than about 76.3 to 76.4 pct Fe. Most of the wüstites therefore appeared to be two-phase at room temperature (see Fig. 4), the percentage of magnetite increasing progressively with increasing oxygen content. Wüstite and magnetite were the only phases ever observed in these oxides. The pure magnetites did not undergo any structural changes on cooling.

As an added point of interest, no oxide which could definitely be considered a homogeneous single-phase structure was obtained having less than 76.73 pct Fe by weight; the stoichiometric compound FeO, if it existed, would correspond to 77.73 pct Fe.

Rates of Self-Diffusion of Iron in Wüstite: Results of the self-diffusion studies on artificially prepared wüstites are summarized in Table III, in which the diffusion conditions, i.e., time, temperature, and atmosphere are given, along with the surface activity and absorption data needed to calculate the self-diffusion coefficients. The fact that results of check runs normally agreed within 25 pct attests to the uniformly high degree of reproducibility which has been achieved in these measurements. Also worthy of note is the observation that at lower temperatures, where diffusion times of greater than 1 hr were used, on occasion, close agreement has been obtained with the results of the shorter time experiments.

Before attempting to analyze the diffusion data for wüstite, it may be well to point out the various possible sources of error in these experiments. These errors are of several types: 1—random errors associated with the uncertainty in measuring the diffusion time or with the failure to duplicate exactly the equilibrium gas composition and temperature during the diffusion anneal; 2—statistical counting errors, as well as those associated with reproduction of the counting geometry and the calculation of the absorption coefficients; 3—errors due to the loss of radioactive iron by vaporization; 4—deviations of a more systematic nature introduced by residual concentration gradients which are not wholly eliminated during homogenization; and 5—completely systematic errors arising from the presence of microscopic inhomogeneities, such as precipitated magnetite particles, or grain boundaries. Since careful control has been exercised over the diffusion and counting procedures, the total error resulting from the first three causes is believed to be relatively small—probably of the order of 10 pct or less. The magnitude of the

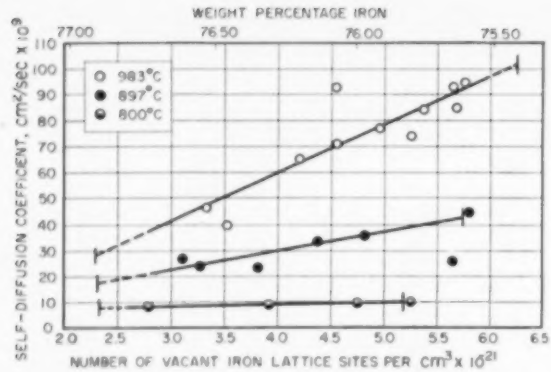


Fig. 6—Dependence of the self-diffusion coefficient of iron in wustite on composition. The short vertical lines represent the limits of the wustite phase field at each temperature, as taken from the work of Darken and Gurry[16]; the number of vacant iron lattice sites per unit volume has been calculated from the deviation from stoichiometric composition (77.73 pct Fe).

other errors is extremely difficult to assess, but a few qualitative remarks may be made.

A large concentration gradient exists at the completion of the oxidation period, the center of the wüstite specimen being richer in iron than the surface layers. If this gradient is not eliminated by homogenization, it will eventually act to retard the inward diffusion of radioactive iron ions and therefore lead to a low value of the self-diffusion coefficient. There is the possibility, however, that in some of the iron-rich wüstites, the residual iron gradient lies in the reverse direction. In any event, it can be assumed that the errors which accompany faulty homogenization are smaller the higher the homogenization temperature, all other factors being equal. The presence of magnetite as a second phase is responsible for systematically low results, as will be evident from the relative rates of diffusion of iron in magnetite and wüstite. Furthermore, the effect of such inhomogeneities is greater in the oxygen-rich wüstites, where the quantity of magnetite precipitated is a maximum, and at the lower diffusion temperatures, where a proportionately longer time is required before the magnetite particles redissolve and the matrix again becomes homogeneous. By taking all these factors into consideration, it has been concluded that the most reliable measurements are those obtained at the highest temperature, 983°C, at compositions lying near the approximate center of the stability range.

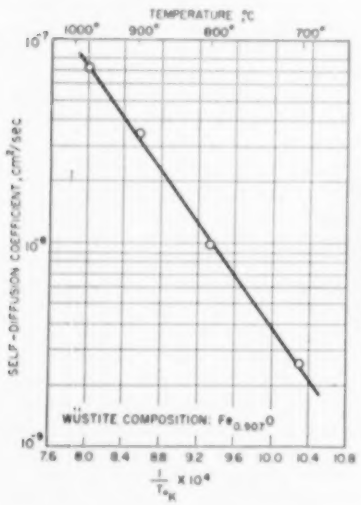


Fig. 7 — Temperature dependence of the self-diffusion coefficient of iron in wustite for oxides having the composition $Fe_{0.907}O$ (76.02 pct Fe).

Variation with Composition: The concentration dependence of the self-diffusion coefficient at 983°, 897°, and 800°C is shown in Fig. 6, in which the average values of $D^*_{Fe^{59}}$ for a given composition are plotted as a function of the calculated number of vacant iron sites per unit volume.† In addition to being a sensitive measure of the deviation from stoichiometric composition, the vacancy concentration has fundamental significance with regard to the transport mechanism in wüstite. For added convenience, however, the corresponding weight percentages of iron in the oxides are also indicated. It is apparent that, over the range of compositions investigated at each temperature, the rate of self-diffusion of iron in wüstite increases continuously as the concentration of vacant iron sites increases. It further appears that this variation is essentially linear, within the precision of the measurements, and that the effect is noticeably greater at 983°C than at 897°C. The lines through the data in Fig. 6 are those given by least squares calculations, whereas the short vertical lines represent the stable limits of the wüstite phase field as taken from the work of Darken and Gurry.

There can be little doubt that the observed increase in the self-diffusion coefficient with vacancy concentration is real, even though the actual magnitudes involved may be rather uncertain. At 983°C, for example, the self-diffusion coefficient increases almost by a factor of four between the iron-rich and oxygen-rich boundaries of the wüstite field. A change of this order is well outside the expected limits of precision at this temperature. The relative change in the diffusion rate for a given change in vacancy concentration seems to be somewhat smaller at 897°C and even smaller still at 800°C. Whether or not this is significant cannot be definitely stated, especially in view of the previous discussion regarding the effect of inhomogeneities on the self-diffusion measurements.

Variation with Temperature: Since the self-diffusion coefficient is rather sensitive to changes in composition, the data accumulated at different temperatures are best compared at a given vacancy concentration. Only one value of the self-diffusion coefficient is available at 699°C and that corresponds to the composition $Fe_{0.907}O$ (=76.02 pct Fe). Accordingly, values of D^* at 983°, 897°, and 800°C have been read from Fig. 6 at this same composition. These are plotted on a logarithmic scale as a function of the reciprocal of the absolute temperature in Fig. 7. The data for this composition are well approximated by the equation

$$D^*_{Fe^{59}} = 0.118e^{-23,700/RT} \qquad [4]$$

between 700°C (973°K) and 1000°C (1273°K). Although there are no data in the literature with which

† The number of vacant cation sites per cu cm, n_v, is given by $n_v = \frac{4\delta}{a_o^3}$, where δ is the deviation from stoichiometric composition, expressed as the deficiency in the number of gram atoms of iron per gram atom of oxygen, and a_o is the edge length of the unit cell in cm. If w_1 and w_2 are the weight fractions of iron and oxygen in the oxide and M_1 (=55.85) and M_2 (=16.00) are the gram atomic weights of iron and oxygen respectively, then $\delta = \left[1 - \left(\frac{w_1}{M_1}\right)\Big/\left(\frac{w_2}{M_2}\right)\right]$ and $n_v = \frac{4}{a_o^3}\left[1 - \left(\frac{w_1}{w_2}\right)\left(\frac{16.00}{55.85}\right)\right]$. The necessary values of a_o as a function of composition are obtained from the work of Jette and Foote.[17]

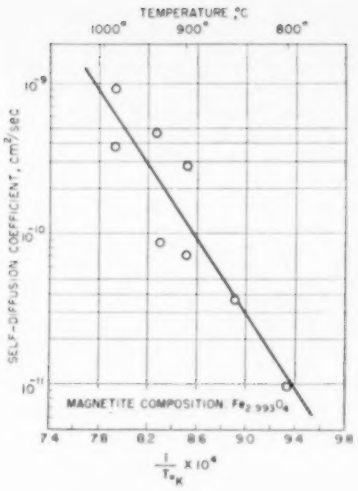
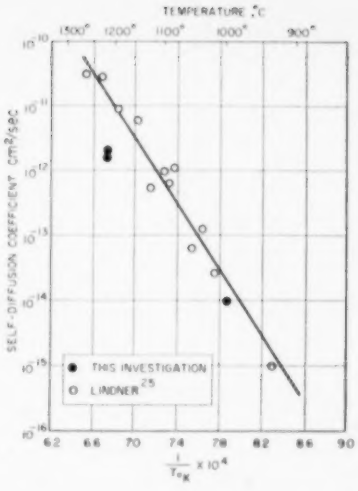


Fig. 8 (left)—The effect of temperature on the rate of self-diffusion of iron in artificially prepared magnetite polycrystals of average composition $Fe_{2.993}O_4$ (72.38 pct Fe).

Fig. 9 (right)—The self-diffusion coefficient of iron in hematite as a function of temperature; the present data refer to natural single crystals of α-Fe_2O_3, Lindner's to pressed and sintered hematite powders.



the present results may be compared, it should be noted that the observed activation energy of 30 kcal per mol is very close to the value often quoted for the oxidation of iron (in air or oxygen).[21] The latter, however, has little significance since it represents a composite quantity which also includes a contribution due to the expansion of the homogeneity range of the wüstite field with rising temperature.[5]

Activation energies for the self-diffusion of iron in wüstite have also been calculated at other compositions, but instead of an expected drop in activation energy at the higher vacancy concentration the opposite trend is observed. This is evident directly from Fig. 6. Such an inconsistency could well be associated with systematic errors of the type previously described.

Rates of Self-Diffusion of Iron in Magnetite and Hematite: The experimental data for artificial magnetite polycrystals and natural hematite crystals are given in Table IV. For the magnetites, the data refer to an average composition corresponding to the formula $Fe_{2.993}O_4$ (=72.38 pct Fe). The scatter in these measurements is fairly appreciable which may indicate that the magnetites were not in complete equilibrium with their atmospheres throughout the entire diffusion period. Nevertheless, if the data are plotted as in Fig. 8, the average values for the self-diffusion coefficient of iron in magnetite can be approximated by

$$D^*_{Fe_3O_4} = 5.2e^{-55,000/RT} \quad [5]$$

over the range from 750° to 1000°C (1023° to 1273°K). The observed activation energy for self-diffusion appears to be substantially greater than the value of 45 kcal per mol found for the growth of magnetite upon iron at temperatures below 570°C.[5] It also differs somewhat from the activation energy for the formation of magnetite on wüstite, as determined by Davies, Simnad, and Birchenall at temperatures between 850° and 950°C.

The self-diffusion data for the natural hematite crystals at 1000° and 1217°C are shown in Fig. 9 along with the more extensive determinations of Lindner[25] on pressed and sintered powder compacts. The present results seem to be somewhat lower; however, when allowance is made for the possibility that the measurements on sintered powders may involve slight contributions from grain boundary and surface diffusion effects, the agreement can be considered satisfactory. Between 950°C (1023°K) and 1300°C (1573°K), Lindner's data‡ for the self-diffusion of iron in α-Fe_2O_3 are represented empirically by the equation

$$D^*_{\alpha\text{-}Fe_2O_3} = 4x10^5e^{-112,000/RT} \quad [6]$$

The present experiments suggest a somewhat smaller activation energy, but since only two temperatures have been investigated, the unusually high value of 112 kcal per mol reported by Lindner must tentatively be accepted. According to Davies, Simnad, and Birchenall, the activation energy for the growth of hematite upon magnetite is only about 53 kcal in the neighborhood of 900°C. A strong indication is thus provided that the growth of the hematite layer depends but little on the diffusion of iron.

It is also interesting to note that, within the uncertainty of the present measurements, the rate of self-diffusion of iron in hematite is independent of the crystallographic direction.

Equilibria Between Wüstite Solid Solutions and H_2-H_2O Atmospheres: The last two columns in Table II give the compositions of the oxides and their coexisting equilibrium atmospheres at the indicated

‡ The constant, D_o, given by Lindner is $4x10^4$ but this is apparently in error by a factor of 10.

Table IV. Self-Diffusion of Iron in Magnetite and Hematite

Specimen No.	Temperature, °C	Time, Sec	Corrected Activity Ratio	μ, Cm^{-1}	D^*, Sq Cm per Sec
Magnetites, Diffused in Water Vapor-Argon Atmosphere					
45	987	$0.3354x10^5$	0.2388	387	92 x10^{-11}
48	987	$0.2178x10^5$	0.3978	387	38 x10^{-11}
52	938	$0.6120x10^5$	0.2473	387	47 x10^{-11}
51	933	$0.5790x10^5$	0.4636	387	8.8 x10^{-11}
47	898	$0.9543x10^5$	0.2547	387	28 x10^{-11}
44	897	$1.523 x10^5$	0.3614	387	7.1 x10^{-11}
49	848	$4.281 x10^5$	0.3183	387	3.6 x10^{-11}
50	799	$17.28 x10^5$	0.3074	387	0.98x10^{-11}
Hematites, Diffused in Pure Oxygen at 1 Atm Pressure					
3*	1217	$9.370 x10^3$	0.6120	385	2.0 x10^{-12}
4†	1217	$9.370 x10^3$	0.6388	385	1.6 x10^{-12}
5*	1000	$6.166 x10^5$	0.97	385	1 x10^{-14}
6†	1000	$6.166 x10^5$	0.97	385	1 x10^{-14}

* Diffusion direction parallel to c-axis of rhombohedral crystal.
† Diffusion direction perpendicular to c-axis.

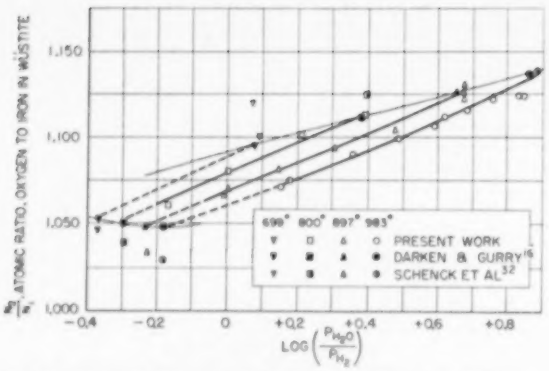


Fig. 10—Equilibria between wustite solid solutions and hydrogen-water vapor atmospheres for compositions within the stable phase field for this oxide. The isotherms give the compositions of the oxides and their coexisting equilibrium gas compositions; included for comparison are data calculated from the work of Darken and Gurry[15] and of Schenck et al.,[32] for the iron-wustite and wustite-magnetite equilibria.

homogenization temperatures. Since it will be found convenient in subsequent calculations to express the oxide compositions in terms of the atomic ratios, N_2/N_1, of oxygen to iron, and the gas compositions in the form P_{H_2O}/P_{H_2} or log (P_{H_2O}/P_{H_2}), the pertinent equilibrium data have been recalculated and assembled in Table V. No corrections have been applied for the deviation from ideal gas behavior because at the temperatures and pressures employed, these corrections amount to considerably less than 1 pct and are probably within the limit of experimental error. Although neither the gases nor the oxides have been analyzed directly, it is believed that the probable error in the calculated water vapor to hydrogen ratios is of the order of ±2 pct or less and that the average oxide compositions calculated from the weight gain are accurate to within ±0.01 wt pct Fe.

Table V. Equilibria Between Wustite Solid Solutions and H_2-H_2O Atmospheres

Specimen No.	Wüstite Composition: Wt Pct Fe	Wüstite Composition: Atomic Ratio Oxygen to Iron, N_2/N_1	Equilibrium Gas Composition: Vol Pct H_2O	Equilibrium Gas Composition: P_{H_2O}/P_{H_2}	Equilibrium Gas Composition: Log P_{H_2O}/P_{H_2}
Temperature = 983°C					
23,24	75.65	1.123	85.0	5.67	0.754
25,26	75.61	1.125	87.5	7.00	0.845
27,28	75.81	1.113	80.6	4.16	0.619
29,30	75.91	1.107	79.5	3.88	0.589
31,32	76.11	1.096	75.4	3.07	0.487
35,36	76.20	1.090	69.6	2.29	0.360
37,38	75.76	1.117	82.6	4.75	0.677
39,40	75.63	1.125	87.2	6.81	0.833
41,42	76.45	1.075	60.2	1.51	0.179
77,78	76.53	1.071	58.9	1.43	0.155
Temperature = 897°C					
55,56	75.65	1.123	82.5	4.71	0.673
57,58	75.97	1.104	74.8	2.97	0.473
59,60	76.14	1.094	67.0	2.03	0.308
61,62	76.35	1.081	58.6	1.42	0.152
63,64	76.55	1.069	50.4	1.02	0.008_6
75,76	75.59	1.127	82.5	4.71	0.673
79,80	76.61	1.066	49.0	0.992	−0.004
Temperature = 800°C					
65,66	75.80	1.114	71.3	2.48	0.395
67,68	76.00	1.102	61.8	1.62	0.209
69,70	76.34	1.082	50.2	1.01	0.004_3
71,72	76.73	1.059	40.7	0.686	−0.164
73,74	76.02	1.101	55.2	1.23	0.090

A series of roughly parallel isotherms are obtained when the appropriate values of N_2/N_1 are plotted against log (P_{H_2O}/P_{H_2}) as in Fig. 10. Also included for comparison in Fig. 10 are the results of similar measurements by Darken and Gurry[15] and by Schenck et al,[32] both of whom employed mixtures of CO and CO_2 to provide suitable oxidizing atmospheres. To convert the P_{CO_2}/P_{CO} ratios given by the latter investigators to the corresponding P_{H_2O}/P_{H_2} ratios, use is made of the equilibrium constant for the water gas reaction, i.e.,

$$K = \left(\frac{P_{CO}}{P_{CO_2}}\right)\left(\frac{P_{H_2O}}{P_{H_2}}\right) \qquad [7]$$

The selected values of K, based on the data of Kassel[34] are: 1.62 at 983°C, 1.30 at 897°C, 0.949 at 800°C, and 0.635 at 699°C. The comparison points plotted in Fig. 10 refer only to the compositions at the extremes of the wüstite phase field.§ It is evident that the present results are in excellent agreement with the work of Darken and Gurry but that the data of Schenck are somewhat discordant.

§ In making these calculations, it was necessary to interpolate the data of Darken and Gurry and of Schenck since these investigators worked at different temperatures than were employed here.

Thermodynamic Calculations: Since wüstite can be regarded as an ionic solid solution, the thermodynamic activity of oxygen in wüstite is proportional to the square root of the equilibrium partial pressure of oxygen in the gas phase. If the activity of oxygen in wüstite is designated as a_2, then

$$a_2 = k\left(\frac{P_{H_2O}}{P_{H_2}}\right) \qquad [8]$$

where the proportionality constant, k, depends upon the temperature and the choice of the standard state. The value of k will be fixed if the activity of oxygen is arbitrarily taken as unity for the wüstite in equilibrium with iron at the particular temperature in question. Adopting this procedure yields the values of k given in Table VI. Although other standard states might have been equally suitable, it was decided to follow the precedent of Darken and Gurry in this selection. The thermodynamic activities of iron in wüstite, a_1, are obtained by the usual Gibbs-Duhem integration, choosing the same standard state as for oxygen. In Table VII the activities of both components are listed for various compositions covering the entire range of the wüstite field at 983°, 897°, and 800°C.

Table VI. Standard States Used in Calculating the Activities of Oxygen and Iron in Wustites at Various Temperatures

Temperature, °C	Iron - Wüstite Equilibrium: N_2/N_1*	P_{H_2O}/P_{H_2}*	P_{O_2} (Atm)†	k in Eq 8
983	1.048	0.658	8.74×10^{-16}	1.52
897	1.048	0.588	2.15×10^{-17}	1.70
800	1.049	0.505	1.61×10^{-19}	1.98
699	1.051	0.430	3.72×10^{-22}	2.34

* Interpolated from the data of Darken and Gurry.[15]

† Based upon equilibrium constants for the dissociation of water vapor obtained from free energy data compiled by Richardson and Jeffes.[33]

The partial molal heats of solution of oxygen and iron in wüstite and the heats of formation of wüstite at various fixed compositions have also been calcu-

lated from the equilibrium data. These data are omitted since they have no direct bearing on the future calculations. It should be mentioned, however, that the average value for the heat of formation of wüstite at 298°K obtained from the present study is −63.5 kcal per mol which is in good agreement with Darken and Gurry's value of −63.7 kcal and with the value $\Delta H_{298} = -63.8 \pm 0.2$ kcal recently quoted by Kelley et al.[19] after a critical appraisal of the existing thermodynamic data for wüstite. This agreement offers some support for the contention that equilibrium has been closely approached in these experiments and that the various approximations involved in calculating the gas and oxide compositions have not introduced significant errors.

Analysis and Discussion

In contradiction to the work of Benard and Coquelle,[25] the kinetic studies of Davies, Simnad, and Birchenall have shown, rather conclusively, that the growth of each of the individual oxide layers is limited by diffusion and not by slow interface reactions. More recently Paidassi[26] has also demonstrated that all three oxide layers grow parabolically with time in the multi-layer scales. This being the case, it now becomes possible, with the aid of the data recorded in Tables III to VII to calculate the rates of growth of the three oxides and to compare these calculated rates with experiment. The basis for such calculations is the well-known theory of oxidation developed by Wagner. Three separate oxidation reactions are to be distinguished: 1—wüstite growing on iron, 2—magnetite growing on wüstite, and 3—hematite growing on magnetite. Since the Wagner theory has heretofore been applied only to systems in which the reaction layer is formed directly on the surface of the metal, an extreme test of its validity and general applicability is at hand. Moreover, if the theory is valid, then the extent to which the calculated growth rates agree with the experimental rate constant data may also furnish a qualitative indication of the relative mobilities of iron and oxygen in the oxides.

Under the assumption that the various component particles (iron = component 1, oxygen = component 2) migrate independently of one another, Wagner[1] has derived the following rate expression for the growth of a single oxide (or sulphide, halide, etc.) layer on a metal substrate:

$$K_r = |z_2| c_2 \int_{a'_2}^{a''_2} \left(\frac{z_1}{|z_2|} D^*_1 + D^*_2 \right) d \ln a_2 \quad [9]$$

$$= z_1 c_1 \int_{a''_1}^{a'_1} \left(D^*_1 + \frac{|z_2|}{z_1} D^*_2 \right) d \ln a_1$$

where K_r, the so-called rational rate constant, represents the number of chemical equivalents of oxide formed per second per square centimeter when the layer of reaction product is 1 cm thick; z_1 and z_2 are the chemical valences of iron and oxygen, c_1 and c_2 are the concentration of the two components in gram atoms per cu cm, D^*_1 and D^*_2 are the respective self-diffusion coefficients, and a_1 and a_2 denote the thermodynamic activities of iron and oxygen in the oxide, the primed and double-primed quantities referring to the conditions at the inner and outer surfaces of the growing oxide layer respectively. It should be noted that K_r, defined as in Eq. 9, does not depend on the choice of the standard state to which the oxygen or iron activities are referred. Of the two equivalent forms of this equation, the first is the more practical since it eliminates the need for the Gibbs-Duhem integration and the errors associated therewith.

Some assumption must obviously be made regarding the relative magnitudes of D^*_1 and D^*_2 in order to evaluate K_r from Eq. 9. Although the relative mobilities of iron and oxygen in the three oxides are known approximately from marker movement studies, this information will be disregarded for the moment, and it will be assumed instead that iron is the only mobile component (besides electrons or electron holes) in each oxide layer. On the assumption that $D^*_1 >> D^*_2$, Eq. 9 can be simplified to

$$K_r = |z_2| c_2 \int_{a'_2}^{a''_2} \frac{z_1}{|z_2|} D^*_1 \, d \ln a_2 \quad [10]$$

The three oxidation reactions will now be considered individually with this equation as a basis.

Oxidation of Iron to Wüstite: If the diffusion of oxygen does not contribute to the growth of the wüstite layer, then since $\ln a_2$ is proportional to 2.303 $\log P_{H_2O}/P_{H_2}$ (see Eq. 8), and $|z_2| = 2$, $z_1 = |z_2| N_2/N_1$, and c_2 is approximately 0.0832 gram atoms of oxygen per cu cm of oxide, Eq. 10 reduces to

$$K_r = 2.303 |z_2| c_2 \int_{a'_2}^{a''_2} D^*_1 \frac{N_2}{N_1} d \left(\log \frac{P_{H_2O}}{P_{H_2}} \right)$$

$$= 0.383 \int_{a'_2}^{a''_2} D^*_1 \frac{N_2}{N_1} d \left(\log \frac{P_{H_2O}}{P_{H_2}} \right) \quad [11]$$

The integration limits correspond to the boundaries of the wüstite phase field at the temperature in question; these are derived from the data of Darken and Gurry (see Table V). The value used for c_2 is based on an average oxide composition of 23.7 wt pct oxygen and an average density of 5.63 g per

Table VII. Thermodynamic Activities of Oxygen and Iron in Wustite

N_2/N_1	P_{H_2O}/P_{H_2}	P_{O_2} (Atm)†	$-\log a_1$	a_1	$\log a_2$	a_2
Temperature = 983°C						
1.048*	0.658	8.74×10^{-18}	0	1	0	1
1.050	0.708	1.01×10^{-15}	0.034	0.985	0.032	1.08
1.060	1.02	2.09×10^{-15}	0.199	0.632	0.193	1.55
1.070	1.41	4.01×10^{-15}	0.351	0.446	0.330	2.14
1.080	1.90	7.30×10^{-15}	0.490	0.323	0.461	2.89
1.090	2.50	1.29×10^{-14}	0.619	0.240	0.580	3.80
1.100	3.22	2.09×10^{-14}	0.740	0.182	0.690	4.90
1.110	4.12	3.43×10^{-14}	0.858	0.139	0.797	6.27
1.120	5.21	5.49×10^{-14}	0.971	0.107	0.899	7.92
1.130	6.43	8.38×10^{-14}	1.075	0.084	0.991	9.79
1.137₅*	7.26	1.06×10^{-13}	1.134	0.074	1.043	11.04
Temperature = 897°C						
1.048*	0.588	2.15×10^{-17}	0	1	0	1
1.050	0.610	2.33×10^{-17}	0.025	0.989	0.016	1.04
1.060	0.815	4.14×10^{-17}	0.151	0.707	0.143	1.39
1.070	1.07	6.84×10^{-17}	0.278	0.528	0.260	1.82
1.080	1.40	1.22×10^{-16}	0.401	0.397	0.377	2.38
1.090	1.82	2.06×10^{-16}	0.525	0.299	0.490	3.09
1.100	2.37	3.51×10^{-16}	0.660	0.219	0.606	4.04
1.110	3.06	5.85×10^{-16}	0.783	0.165	0.719	5.24
1.120	3.90	9.49×10^{-16}	0.899	0.126	0.822	6.64
1.126*	4.46	1.24×10^{-15}	0.957	0.110	0.880	7.59
Temperature = 800°C						
1.049*	0.505	1.61×10^{-19}	0	1	0	1
1.050	0.514	1.67×10^{-19}	0.021	0.991	0.008	1.02
1.060	0.630	2.51×10^{-19}	0.101	0.792	0.097	1.25
1.070	0.776	3.81×10^{-19}	0.198	0.634	0.188	1.54
1.080	0.968	5.93×10^{-19}	0.301	0.500	0.283	1.92
1.090	1.22	9.42×10^{-19}	0.410	0.389	0.384	2.42
1.100	1.61	1.64×10^{-18}	0.542	0.287	0.504	3.19
1.110	2.17	2.99×10^{-18}	0.686	0.206	0.635	4.31
1.112*	2.44	3.76×10^{-18}	0.741	0.181	0.684	4.83

* Limits of the wüstite phase field as given by Darken and Gurry.[16]
† See dagger footnote, Table VI.

Table VIII. Comparison Between the Experimental Scaling Rate Constants and Those Calculated from the Wagner Equation

Temperature, °C	Calculated Rational Rate Constant, K_r, Equivalents Per Cm Per Sec	Parabolic Scaling Constant, K_p, G-Cm^{-2}-Sec$^{-1/2}$	
		Calculated	Experimental
A. Iron to Wüstite			
983	2.8 x10^{-8}	7.7 x10^{-4}	8.2 x10^{-4}
897	1.1 x10^{-8}	4.8 x10^{-4}	5.0 x10^{-4}
800	0.25x10^{-8}	2.3 x10^{-4}	2.3 x10^{-4}
B. Wüstite to Magnetite			
1100	9.2 x10^{-9}	1.7 x10^{-4}	1.8 x10^{-4}
1050	4.1 x10^{-9}	1.1 x10^{-4}	1.3 x10^{-4}
1000	1.4 x10^{-9}	0.67x10^{-4}	0.90x10^{-4}
C. Magnetite to Hematite			
1100	1.7 x10^{-12}	2.2 x10^{-6}	1.0 x10^{-4}
1000	2.1 x10^{-14}	2.4 x10^{-7}	4.8 x10^{-5}

cu cm. Although the average composition of the wüstite layer does depend slightly on the temperature of oxidation, no significant error is introduced by assuming c_2 to be constant over the range from 800° to 1000°C. Eq. 11 is integrated graphically from plots of $D^*_1 N_2/N_1$ vs log P_{H_2O}/P_{H_2} which are prepared from the data given in Fig. 6 and Table V. The resulting values of the rate constants for the growth of wüstite on iron at 983°, 897°, and 800°C are listed in Table VIIIA.

Oxidation of Wüstite to Magnetite: It is assumed that the self-diffusion coefficients reported here (Eq. 5) for iron in magnetite are sufficiently close to the effective averages that the variation with concentration may be neglected. Thus, with $z_1 = 8/3$ and $c_2 = 0.0897$ gram atoms of oxygen per cu cm of Fe_3O_4, the rational rate constant for the growth of magnetite on wüstite becomes

$$K_r = 2.303 \times \frac{8}{3} \times 0.0897\, D^*_1 \int_{a'_2}^{a''_2} d \log a_2 = 0.551\, D^*_1 \log \left(\frac{a''_2}{a'_2} \right) \quad [12]$$

provided that the diffusion of iron in magnetite is rate-controlling and that there is no contribution due to oxide ion diffusion. An average magnetite composition of 27.72 wt pct oxygen and a density of 5.18 g Fe_3O_4 per cu cm have been used in computing c_2. The oxygen activities corresponding to the limits of the magnetite field are obtained from the work of Darken and Gurry. A slight complication arises because of the fact that the available activity data refer to the temperature range from 1100° to 1400°C while self-diffusion coefficients are known only between 800° and 1000°C. The rate constants have therefore been calculated for the intermediate temperature range of 1000° to 1100°C so as to avoid excessively large extrapolations (see Table VIIIB).

Oxidation of Magnetite to Hematite: If this process takes place at a pressure of 1 atm of oxygen and if D^*_1 is again assumed independent of concentration, then since $z_1 = 3$ and $c_2 = 0.0983$ gram atoms of oxygen per cu cm of Fe_2O_3, Eq. 10 becomes

$$K_r = 2.303 \times 3 \times 0.0983\, D^*_1 \int_{a'_2}^{a''_2} d \log a_2 = -0.679\, D^*_1 \log a'_2 \quad [13]$$

subject to the initial assumption that $D^*_1 >> D^*_2$. The oxygen concentration in hematite has been calculated for the stoichiometric composition (30.06 wt pct oxygen) using an oxide density of 5.24 g per cu cm. As in the previous example, the magnetite-hematite equilibrium given by Darken and Gurry requires extrapolation. The rate constants for the growth of hematite on magnetite have been calculated only at 1000° and 1100°C, at which temperatures $D^*_1 \cong 1 \times 10^{-14}$ sq cm per sec and 1×10^{-12} sq cm per sec respectively (see Fig. 9).

To test the various assumptions upon which the above calculations are based, a comparison will now be made with rate constant data obtained directly from kinetic studies. The recent measurements of Davies, Simnad, and Birchenall have been selected for this purpose. These investigators followed the course of oxidation of iron and of the lower oxides, wüstite and magnetite, by conventional weight gain techniques, finding in each case that the parabolic rate law was closely obeyed. The experimental rate constants reported by Davies, Simnad, and Birchenall are defined, accordingly, by the equation

$$\frac{W}{A} = K_p t^{1/2} \quad [14]$$

where W is the weight increase, i.e., the number of grams of oxygen added, A is the surface area of the specimen in square centimeters, t is the time in seconds, and K_p is the familiar parabolic scaling constant, having the dimensions g-cm^{-2}-sec$^{-1/2}$. It can be shown[1] that K_p and K_r, defined as in Eq. 9, are related by the expression

$$K^2_p = \frac{2M_2}{|z_2|} f_2 \rho K_r \quad [15]$$

M_2 being the weight of one gram atom of oxygen, and f_2 the weight fraction of oxygen in the growing oxide layer, the density of which is ρ; hence with $M_2 = 16$ and $|z_2| = 2$

$$K^2_p = 16 f_2 \rho K_r \quad [16]$$

Using this relationship, the calculated and experimental rate constants may be reduced to a common basis.

Although Eq. 16 holds for the reaction between oxygen and iron, it does not apply without qualification to the oxidation of the oxides themselves, because the parabolic scaling constant refers only to the oxygen which has been taken up by the specimen from the gas phase, whereas, by definition, the rational rate constant is a measure of the total quantity of oxygen in the growing oxide layer, regardless of its origin. When a metal is oxidized to form a single-layer scale, the weight gain and the amount of oxygen in the scale are identical, provided solubility in the underlying metal can be neglected. However, when one oxide is converted to a higher oxide only a fractional part of the oxygen in the product is actually derived from the gas phase. This fraction is calculable from the stoichiometric relations between the phases and represents a correction factor, α, which must be applied to K_r in Eq. 16, i.e.,

$$K^2_{p_{calc.}} = 16 f_2 \rho \alpha K_r \quad [17]$$

The value of α is unity for the growth of wüstite on iron; for the oxidation of wüstite to magnetite, α varies between approximately 1/5 and 1/7, depending on the composition of the starting material, while for magnetite being oxidized to hematite, α is very nearly 1/9.

The parabolic rate constants for the oxidation of iron to wüstite, calculated from K_r according to Eq. 17 are listed in Table VIIIA, along with the experimental values of K_p obtained from the data of Davies, Simnad, and Birchenall. The latter actually correspond to overall rate constants for the reaction between iron and oxygen gas at 1 atm pressure. Even in a pure oxygen atmosphere, however, the wüstite phase constitutes upwards of 95 pct of the growing scale layer.[5, 20] Thus, despite the simultaneous formation of the higher oxides, the total or overall scaling rate is not significantly greater than the rate of growth of the wüstite layer alone, and a direct comparison is therefore permissible. It is evident from Table VIIIA that the rate constants calculated from the Wagner equation are in excellent agreement with the experimental rate constant data. Since it has been assumed that iron is the effective diffusing component in wüstite, and since the validity of this special assumption has been established by independent marker movement studies, the agreement between the calculated and observed rate constants may be taken as direct experimental confirmation for the Wagner theory.

One of the assumptions which has been made in the derivation of the Wagner equation is that the transference numbers of the ions are extremely small in comparison to the transport number for electrons. This is a perfectly valid assumption for most transition metal oxides, and particularly for the oxides of iron, which are known to be almost purely electronic conductors. The transference number of the cations in wüstite can be calculated, at least approximately, with the aid of the Nernst-Einstein relation,[6, 8]

$$\sigma \tau = \frac{n z^2 e^2 D^*}{kT} \qquad [18]$$

where σ represents the specific electrical conductivity of the oxide, τ is the transference number of the ion in question, n the number of cations per cubic centimeter, z the valence of the charge carrier, and D^*, its self-diffusion coefficient. At 1000°C (1273°K) and an oxygen pressure of approximately 4×10^{-15} atm, Wagner and Koch's[20] experimental value for σ is 107 ohm^{-1}-cm^{-1}; under these same conditions, $n \cong 4.88 \times 10^{22}$, while D^*, obtained from the present study, is roughly 6.4×10^{-7} sq cm per sec. Hence, with the appropriate values of the electronic charge, e, and the Boltzmann constant, k, the transference number of Fe^{++} ions in wüstite is found to be approximately 2×10^{-4}. This may be compared, as to order of magnitude, with the experimental value of 5×10^{-4} obtained by Gundermann and Wagner[27] for the transport number of Cu^+ ions in Cu_2O at 1000°C.

The Wagner treatment also assumes that the ions and electrons migrate independently of one another and that the Nernst-Einstein equation, relating the ionic mobilities and the respective self-diffusion coefficients, is satisfied. These fundamental assumptions imply virtually complete dissociation of the vacancies and electron holes, and the absence of large deviations from ideal solution behavior of the Debye-Hückel type. From their work on the oxidation of copper, Bardeen, Brattain, and Shockley[28] have inferred that only a small fraction of the defect centers in cuprous oxide are associated to form vacancy-hole pairs at temperatures near 1000°C. However, the agreement which has been obtained between the experimental rate constants for the oxidation of iron and those calculated from the self-diffusion and activity data, does not, in itself constitute proof that diffusion in wüstite also occurs largely by the mechanism of dissociated vacant sites. In the oxygen-rich wüstites, for example, the concentration of vacancies and electron holes is so great that on the average, every Fe^{++} ion must have at least one nearest-neighbor site which is vacant, and moreover, each vacancy must have at least two Fe^{+++} ions as nearest neighbors. In other words, virtually complete association, rather than dissociation, would be expected purely on geometrical grounds. There are of course additional factors to be considered, such as the electrostatic attraction between the positive electron holes and the cation vacancies, the latter having an effective negative charge; this attraction also promotes the formation of vacancy-hole complexes.

If these complexes were mobile to any appreciable extent, their motion would contribute to the measured self-diffusion coefficient but not to the conductivity, since the associated defect centers are electrically neutral.[6] This would then lead, substantially, to a breakdown of the Einstein relationship.[26] Hence, in the absence of the necessary conductivity and transport number data with which to test the validity of the Einstein relationship directly, it cannot be established with certainty whether or not an appreciable fraction of the observed diffusion in wüstite occurs through electrically neutral "trapped" vacancies. On the other hand, the fact that the Einstein relationship leads to a reasonable value for the transference number of Fe^{++} ions in wüstite may be taken as evidence that both diffusion and conductivity in this oxide are indeed due to the same mechanism, e.g., the migration of free or dissociated vacancies.

If this assumption is correct, and if at the same time there exists an appreciable fraction of neutral, associated centers, then the mobility of these complexes must be much smaller than that of the free vacancies. This means, in turn, that the effective number of vacant sites may be considerably less than the number calculated from the deviation from stoichiometric composition. Furthermore, since association is favored at the higher vacancy concentrations and at lower temperatures, the effective number of vacancies might be expected to vary in exactly the opposite sense. Arguments of this kind could conceivably be used to explain the observed changes in slope of the D^* vs vacancy concentration curves (Fig. 6) with temperature. As previously mentioned, however, the diffusion data are not considered precise enough to justify much speculation on this point. The subject is of sufficient general importance to warrant a more detailed study of the diffusion and conduction processes in wüstite, especially at lower temperatures than have been employed in this investigation. It might also prove helpful to examine Kelley's[10] suggestion regarding the presence of an ordered arrangement of vacancies in wüstite; this should be amenable to direct experimental proof by X-ray techniques.

The basic assumption has also been made by Wagner that the oxide growing on the metal substrate has properties identical with those of the homogeneous bulk oxide of the same chemical composition. Wagner and his coworkers[1] showed this to be true for the growth of Ag_2S on silver. Supporting evidence has also been provided by the more recent work of Moore and Selikson,[29] who studied the self-diffusion of copper in bulk specimens of Cu_2O, obtaining essentially the same results as previously

reported by Castellan and Moore,[41] and by Bardeen, Brattain, and Shockley, for self-diffusion in the cuprous oxide layer growing on the surface of the metal. It is probable that this assumption is fulfilled whenever the layer of reaction product reaches a thickness such that the substrate no longer exerts any appreciable influence on its properties.[42, 43]

In the derivation of the rate equation (Eq. 9) Wagner also found it necessary to assume that the product oxide is nearly stoichiometric in composition. This was done in order that the sum of the equivalents of metal and nonmetal passing a given plane per unit time would be the same at any distance through the scale layer. If this condition is to be satisfied in wüstite, where the vacancy concentration and the self-diffusion coefficient increase rather rapidly in traversing the scale, there must be a corresponding decrease in the activity gradient between the inner and external surfaces of the wüstite layer. Experimental proof for this is lacking, but could be obtained fairly readily now that the activities are known as a function of composition. Attention should also be called to the fact that in carrying out the rate constant calculations for wüstite, z_i has been allowed to vary with distance relative to $|z_e|$. This approximation does not seem to have introduced any serious error.

The interpretation of the rate constant calculations for the oxidation of wüstite (to magnetite) is complicated slightly by the apparent conflict which exists regarding the relative mobilities of iron and oxygen in Fe_3O_4. Actually, however, close agreement has again been obtained between the calculated and experimental scaling rates for this reaction (see Table VIIIB). Such agreement seems to indicate that the diffusion of oxygen contributes only slightly to the growth of the magnetite layer, and if so, represents additional confirmation for the Wagner theory. This conclusion is consistent with the accepted structural model for Fe_3O_4 given by Verwey,[10-12] which provides a convenient mechanism for the diffusion of iron (through lattice vacancies), but not for oxygen. Still, an objection to this general picture seems to have been raised by the marker movement experiment of Davies, Simnad, and Birchenall. On the basis of the observed marker shift during the oxidation of wüstite to magnetite, these investigators originally concluded that the mobilities of oxygen and iron in Fe_3O_4 were of comparable magnitude at temperatures near 900°C. Since publication of this result, however, it was realized that the observed marker movements were misinterpreted (see asterisk footnote, p. 828), and it now appears that the marker measurements are also overwhelmingly in favor of iron ion diffusion as the controlling factor in the growth of the magnetite layer. Thus, within the uncertainty of the diffusion and rate constant measurements, the Wagner equation again gives acceptable agreement with experiment.

A few additional remarks concerning the temperature dependence of the rate constant for this reaction may be in order. Structural considerations alone make it probable that the activation energies for the self-diffusion of iron and oxygen in magnetite differ quite significantly. Nevertheless, a critical temperature range may exist within which the relative mobilities or diffusivities of the two components are approximately equal. Therefore, if iron is the dominant diffusing component above this critical temperature, oxygen must assume this role at lower temperatures, and vice versa. In either case, a shift from one diffusion-controlled process to another requires that there be a corresponding change in the activation energy for the oxidation reaction on passing through this critical range. The experimental rate constant data[5] for the oxidation of wüstite between 850° and 950°C do not indicate any such trend; however, in order to be conclusive, rate constant and mobility data are needed over a much wider temperature range.

As seen in Table VIIIC, the assumption that iron is the only mobile component in α-Fe_2O_3 leads to a discrepancy of approximately two orders of magnitude between the calculated and experimentally determined rate constants for the oxidation of magnetite. This lack of agreement is entirely consistent with expectation and strongly supports the earlier proposals of Bevan, Shelton, and Anderson,[28] and Davies, Simnad, and Birchenall with regard to transport predominately by oxygen ions or oxide ion vacancies. By taking oxygen as the effective diffusing component in hematite, and reversing the calculations, the average self-diffusion coefficient, D^*_2, can be evaluated from the experimental rate constant data. Thus D^*_2 is found to be 3.6×10^{-9} sq cm per sec at 1100°C and 5.9×10^{-10} sq cm per sec at 1000°C; at these same temperatures the measured values of D^*_1 are about 1×10^{-12} and 1×10^{-14} respectively. Nevertheless, no direct conclusions can be drawn regarding the validity of the Wagner approach. This must await the actual determination of the transference numbers or of the rates of self-diffusion of oxygen in hematite.

Summary

1—Techniques have been developed for the preparation of bulk, homogeneous wüstites and magnetites of controlled composition by the direct oxidation of high-purity iron in atmospheres of constant, known, oxidizing potential.

2—The rates of self-diffusion of iron in the large-grained, polycrystalline wüstites have been determined over a range of compositions and temperatures, using the decrease in surface activity method with Fe^{55} as the tracer isotope. Within the precision of the measurements at each temperature, the self-diffusion coefficient for iron in wüstite is found to increase in linear fashion with increasing deviation from stoichiometric composition. At 983°C, for example, a four-fold increase is observed between the iron-rich and oxygen-rich boundaries of the wüstite phase field. This observation essentially confirms the view that the diffusion mechanism in wüstite involves the exchange of cation vacancies with normal lattice ions. Between 699° and 983°C the activation energy for the diffusion process is approximately 30 kcal per mol for compositions lying near the middle of the stability range.

3—Similar measurements have also been made on artificially prepared magnetites at temperatures between 799° and 987°C and on natural hematite single crystals at 1000° and 1217°C. The self-diffusion data obtained for hematite compare favorably with the results of more extensive experiments by Lindner on sintered powder compacts. The activation energy for the self-diffusion of iron in magnetites of average composition $Fe_{2.998}O_4$ is approximately 55 kcal per mol; for α-Fe_2O_3 the activation energy is at least 100 kcal per mol and probably greater.

4—At temperatures between 1000° and 1217°C the rate of self-diffusion of iron in single crystals of

α-Fe_2O_3 appears to be independent of the crystallographic direction.

5—The reactions between wüstite solid solutions and H_2-H_2O atmospheres have been investigated in the range from 699° to 983° in order to establish the compositions of the oxides and their coexisting equilibrium atmospheres.

6—From these data the thermodynamic activities of iron and oxygen in wüstite have been calculated at various round compositions within the wüstite phase field. The partial molal heats of solution of iron and oxygen in wüstite and the heats of formation of wüstite have also been evaluated. The observed value $\Delta\bar{H}_{298°K} = -63.5$ kcal per mol is in good agreement with existing thermodynamic data for this oxide.

7—Using the self-diffusion and thermodynamic data, and applying the theoretical rate equations developed by Wagner, rate constants have been calculated for the growth of wüstite on iron, magnetite on wüstite, and hematite on magnetite, under the assumption that iron is the only diffusing component (in addition to holes or electrons) in each of the growing oxide layers.

8—The calculated scaling constants are compared with experiment and it is shown that the applicability of the Wagner theory is perhaps even more general than previously suspected. Not only has acceptable agreement been obtained between the calculated and experimentally determined rate constants for the growth of an oxide layer on a metal substrate, e.g., wüstite on iron, but the same is true for the conversion of one oxide to another, e.g., wüstite to magnetite.

9—Except for some disagreement regarding the relative contributions of iron and oxygen diffusion to the growth of magnetite, the mechanism of the multi-layer scaling of iron proposed by Davies, Simnad, and Birchenall is also substantiated by these observations. This mechanism is now thought to involve the outward migration of iron in the wüstite and magnetite layers and the inward diffusion of oxygen in the hematite layer.

10—The transference number of Fe^{++} ions in wüstite is estimated, from self-diffusion and electrical conductivity data, to be approximately 2×10^{-4} at 1000°C.

11—Previously reported effects of the α-γ transformation temperature on the kinetics of the oxidation of iron must be attributed to reactions occurring at the metal-scale interface since there are no structural changes, and therefore no discontinuities in the rates of self-diffusion in the oxides at this temperature.

Acknowledgments

This work was initiated under a graduate fellowship generously granted to one of us by the Westinghouse Electric Co., and completed under the sponsorship of the Office of Naval Research. The authors greatly appreciate the assistance offered by H. M. Schadel, Jr. in the construction of the apparatus, and by W. E. Bostrom and J. M. Ferrin who performed the radiochemical analyses.

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Technical Note

High Temperature Corrosion in Nickel-Chromium Alloys

by Norman Spooner, John M. Thomas, and L. Thomassen

NI-CR and some Ni-Cr-Fe alloys, when used as electrical resistance heating elements in reducing atmospheres, at times suffer rapid breakdowns due to so-called "green rot." These reducing atmospheres are most frequently used in bright annealing and heat-treating furnaces which are kept for long periods of time at 1500° to 1800°F. The green rot is a preferential oxidation of the chromium in the alloy to such an extent that the remaining metal frequently becomes ferromagnetic. The Curie point (magnetic transition point) at room temperature for a pure Ni-Cr alloy is known to be at about 7 pct Cr.[1] This represents a severe loss in chromium for one popular grade of resistance alloy, which is nominally 80 pct Ni-20 pct Cr. The formation of oxides along the grain boundaries makes the ribbon brittle and gives the fracture a green, earthy appearance—hence the name.

The authors have studied this phenomenon, simulating the industrial conditions by heating resistance ribbons in various reducing atmospheres, such as moist hydrogen or the atmosphere specified in the ASTM test.[2] This atmosphere contains 16 pct H_2, 10 pct CO, 4 pct CO_2, 1 pct CH_4, 1.5 to 2.5 pct H_2O, balance N_2.

Little success was had in producing severe corrosion with the commercial 80 pct Ni-20 pct Cr alloys. It had been noticed, however, that 90 pct Ni-10 pct Cr alloy wires deteriorated very rapidly when placed in the bottom of narrow thermocouple protection tubes. The bottoms of the tubes with the wires were heated in air. This took place both in porcelain tubes and in Inconel* tubes either with the cold end open or loosely stoppered with asbestos. On examination the wires showed microstructures which would be classified as green-rot corrosion.

* Inconel is a heat and corrosion resistant alloy manufactured by the International Nickel Co. and has a nominal composition of 78 pct Ni, 14 pct Cr, balance Fe.

Subsequent investigations with various alloy wires confirmed the observation that corrosion occurred in some wires, including 80 pct Ni-20 pct Cr alloys, much more rapidly in such tubes than had occurred previously in test atmospheres mentioned above.

When 90 pct Ni-10 pct Cr alloys are oxidized with an abundant air supply, the oxide coat consists of both nickel and chromium oxides. In this case thermodynamic equilibrium between the oxides is not established.

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However, when oxidized 90 pct Ni-10 pct Cr alloy specimens were heated to 1500° to 1800°F inside small diameter tubes, the oxide coat transformed to a bright metallic outer layer of nickel or nickel-rich alloy, beneath which appeared a green oxide, followed by intergranularly attacked metal. The obvious explanation is that in the narrow tubes, thermodynamic equilibrium is being established according to the equation

$$NiO + Cr \text{ (in alloy)} \rightarrow Ni + Cr_2O_3$$

This reaction is favored due to the fact that the oxygen pressure over nickel oxide is more than 10^{10} times the oxygen pressure over the green chromium oxide. The initial oxygen in the tubes is depleted very rapidly by oxidation of the wire and of the tube, if it is metallic. A confirmation of the occurrence of the reaction, reduction of NiO by the chromium in the alloy, was obtained by putting oxidized nickel foil into an evacuated quartz tube along with a piece of bright 90 pct Ni-10 pct Cr alloy ribbon, and heating the tube at 1820°F for a number of hours. The nickel oxide on the foil was completely reduced to pure nickel, leaving a bright foil. The 90 pct Ni-10 pct Cr alloy became strongly magnetic and showed the typical green-rot structure. Weights of the samples before and after testing showed the weight loss of the foil to approximately equal the weight gain of the ribbon. Evidently the bottom of long, narrow protection tubes, stoppered or not, may under certain conditions act just as the sealed quartz tubes in respect to being a confined space in which oxygen is not freely replenished. This condition of oxygen depletion can be prevented by introducing a small amount of air into the bottom of the tube.

Many conditions becloud the green-rot phenomenon, such as carburization, sulphidization, and the presence of other corrosive agents. However, these experiments have shown that the basic reaction is a case of internal oxidation which can occur simply by adjusting the oxygen pressure to a low enough level so that the atmosphere will leave the nickel intact and oxidize the chromium. The action of the other agents in commercial atmospheres can then be taken up as individual cases.

From these and numerous other tests completed to date or still in progress, it is believed that a more critical evaluation of electrical resistance alloys for their resistance to green-rot corrosion can be made. A much better understanding of the mechanism for this type of corrosion should also result. A more complete report on these experiments will be published later.

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Correction

In the May 1953 issue: TP 3521E *Discussion: Solubility of Carbon and Oxygen in Molybdenum* by W. E. Few and G. K. Manning, discussion by N. A. Gokcen: p. 747, first column, the fifth, sixth, and seventh lines should be the first, second, and third lines, followed by the present first, second, third, fourth, eighth, ninth, and tenth lines.

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aime NEWS

President Fletcher Visits Australia

Andrew Fletcher, left, presented the AIME Legion of Honor Medal to W. E. Wainwright, right, Honorary Treasurer of the Australasian Institute of Mining and Metallurgy, at the luncheon given by the Council of the AIMM. Looking on is M. A. Mawby, President of AIMM. Mr. Fletcher visited Australia in connection with the Fifth Empire Mining and Metallurgical Congress. Prior to his departure, he was presented with a certificate of Honorary Membership in the Australasian Institute.

AIME President Ends Six Weeks' Tour

President Fletcher returned to New York on May 6 after a six weeks' trip most of which was spent in Australia. He attended the Fifth Empire Mining and Metallurgical Congress in that country and gave several talks. Before leaving the country he was made an Honorary Member of the Australasian Institute of Mining and Metallurgy. On his return to the USA, Mr. Fletcher attended AIME meetings in San Francisco, Reno, Salt Lake City, Denver, Golden, and Casper. Within a week after his return he departed for Tulsa to attend a meeting of the Mid-Continent Section, AIME, and of the Board of Directors. After a tour of the International Petroleum Exposition, he stopped for a meeting of the Tri-State Section at Joplin, addressed the students at Rolla, attended a meeting of the St. Louis Section, and was honor guest of the Chicago Section on President's Night, May 23.

Hold Second Student Conclave at Rolla, Mo.

In spite of inclement weather, the second annual joint meeting of the St. Louis Section and Student Chapters was very successful. Some 80 students and guests gathered at the Missouri School of Mines, Rolla, Mo. to hear views on different types of employment. C. L. Wilson, dean of the Missouri School of Mines, addressed the conclave at the welcoming luncheon.

Frank Lindeman, Jr., manager of the producing dept., Stanolind Oil & Gas Co., spoke on employment in large companies and O. W. Bilharz, president of the Bilharz Mining Co., discussed careers with small firms and private or individual enterprises.

Opportunities for foreign employment was the topic of L. H. Hart's talk. Mr. Hart is resident engineer, American Smelting & Refining Co. Representing the government was LeRoy Williams, project engineer of the USGS.

An afternoon program was arranged for the WAAIME. Dinner was held at the Edwin Long Hotel and Joseph Desloge, Jr. presented a film, *The Desloge Expedition Down the Colorado River*, which was viewed with interest by all.

Board Approves Final AIME Budget for 1953

At its meeting in Tulsa, May 13, the Board of Directors approved the final budget for 1953. This indicated an income of $651,000, compared with actual income of $593,381 in 1952; and expenses of $608,100, compared with actual expenses of $575,315 in 1952. Of the 1952 surplus, $10,000 was returned to the Special Fund for Publications which had been drawn upon during the years of serious deficits, and of the anticipated surplus for 1953, $30,000 is earmarked for return to this reserve fund. The Fund will still remain less than half of what it was before it was tapped to meet the serious deficits of 1947 to 1949, amounting, in those three years, to $182,000.

RESEARCH IN PROGRESS

Research personnel are reminded of the Institute of Metals Div. Research in Progress session planned for the Fall Meeting in Cleveland. Abstracts of proposed papers not exceeding 200 words in length are to be submitted to Institute headquarters prior to Aug. 1, 1953, for inclusion in the September issue of JOURNAL OF METALS. Abstracts not received in time for publication in the September issue may, nevertheless, be presented if received prior to Sept. 15, 1953, according to B. L. Averbach, IMD Program Committee.
The Program Committee urges those interested to avail themselves of the opportunity of participation in this program in order that new research information be presented for discussion.

Sam Naismith, Blast Furnace, Coke Oven and Raw Materials Committee Chairman, speaking informally at the Fellowship Dinner, found a receptive audience.

Steelmen lining up at the registration desk made the meeting the second largest in conference history. More than 1400 persons attended the gathering.

Past Chairman Al Sommer receives perpetual registration certificate and clock from J. J. Golden, National Open Hearth Committee Chairman.

Iron & Steel Conference Technical Sessions Attract Capacity Audiences

More than 1400 Gather at Buffalo; Next Blast Furnace And Open Hearth Meeting to Be Held in Chicago Apr. 5 to 7, 1954

THE second largest combined meeting of the Blast Furnace, Coke Oven and Raw Materials Committee, and the National Open Hearth Steel Committee was held at the Statler Hotel in Buffalo, Apr. 20 to 22, 1953. Total attendance was over 1400, with 377 registering for the Blast Furnace sessions. Most of the registrants never realized how close the meeting came to being postponed, or held in another city. It all came about when the hotel staffs in Buffalo went out on strike the week before the meeting, and alternate plans had to be made almost overnight. Fortunately, a settlement was reached and everything settled back to normal.

Many old acquaintances were renewed and many new friends were made during the three-day conference. It is impossible to estimate the effect in the steel industry of the increased knowledge of the registrants as a result of the meeting. The large registration leads to the conclusion that there must be some good results, or companies would not continue to send more operating men each year.

This year, for the first time, a JOURNAL OF METALS Award was made available to the Blast Furnace, Coke Oven and Raw Materials Committee. This will be presented annually for the best paper submitted by the announced conference paper deadline. The 1953 award was made at the Fellowship dinner to F. M. Stephens, Jr., Benny Langston, and A. C. Richardson, Battelle Memorial Institute for their excellent and timely paper *The Reduction-Oxidation Process for the Treatment of Taconites*. Other awards made at the dinner were the McKune Award to J. H. Flaherty, Jr., Jones & Laughlin Steel Corp., for his paper *Quality Control in the Production of High Sulphur Open Hearth Steels*, and the Open Hearth Conference Award to A. W. Fastabend, American Steel Foundries, for his paper *The Effect of Reduced Aluminum Deoxidation on Cast Steel*.

Chairman Sam Naismith presided at the annual luncheon of the Blast Furnace, Coke Oven and Raw Materials Committee held Tuesday, April

J. J. Golden, presiding at the Fellowship dinner, performed his tasks with finesse. Seated left to right are Al Sommer, Ken McCutcheon, Dan Loughrey, W. H. Durrell, and J. J. Golden.

Guest speaker William H. Durrell recounted the history of the Labrador iron ore development from discovery to current status.

First Annual JOURNAL OF METALS Award was presented by Sam Naismith to F. M. Stephens, Jr., and Benny Langston. A. C. Richardson, third co-author, was unable to attend. Their paper, *Reduction-Oxidation Process for the Treatment of Taconites* appears in this issue.

21. He introduced as guests J. J. Golden, National Open Hearth Committee Chairman, and E. H. Robie, Secretary of AIME. Chairmen of the various conference committees were called upon to present their reports. Naturally, one of the most interesting reports was that the committee treasury was continuing to grow.

The varied interests of registrants led to the holding of simultaneous sessions. Even with this division, all sessions were held with capacity audiences. In some instances, it was standing room only. When an engineer stands at a technical meeting, it must be interesting!

At the annual Fellowship dinner on Tuesday evening, J. J. Golden, Chairman of the National Open Hearth Committee presided. He introduced Sam Naismith, Chairman of the Blast Furnace, Coke Oven and Raw Materials Committee. After a brief address, Mr. Naismith presented the first annual JOURNAL OF METALS Award. Lou Berner was asked to take a bow as incoming Chairman of National Open Hearth Steel Committee. John Golden then presented a Past Chairman's Certificate, perpetual registration, and a suitably inscribed electric clock to Al Sommer. There was some interchange of remarks concerning the advantages of being a Past Chairman—he could sit back and enjoy the meeting while the chairman worked. Chairman Golden then presented the McKune Award and Open Hearth Conference Award.

Toastmaster Dan Loughrey, obviously deciding that the meeting had been too serious for too long, proceeded to change the pace. Unfortunately, his remarks cannot be reprinted here, but many of them will be passed around whenever steelmen congregate. Even the metallurgists and blast furnace men, who bore the brunt of some of the remarks, enjoyed the good natured joking. Dan Loughrey will be sought after as Toastmaster for many another meeting.

The Toastmaster then introduced guest speaker William H. Durrell, general manager of Iron Ore Co. of Canada, Montreal. He discussed the discovery of the Labrador iron ore deposits, and the project underway to mine and ship the ore. Mr. Durrell dwelt on the strategic importance of availability of iron ore on the North American continent. However, to ship the ore quickly and in volume, he stated that the development of the St. Lawrence Seaway project was vital. "During wartime, Labrador ore, moving along the St. Lawrence . . . to the Great Lakes, would be relatively easy to protect. Coastal plants depending on water borne imports were a casualty of the last war, and millions of tons of ore had to be shipped overland to the coast from Lake Superior ranges," he said.

No account of the Fellowship dinner would be complete without acknowledging the splendid entertainment provided by the Stelco Male Chorus of the Steel Co. of Canada, Ltd., under the direction of Roderick A. Shepherd. Their reception by the 800 attending the dinner was proof that they would always be welcome by the group.

The last day of the Conference, Wednesday, was devoted to simultaneous plant visits to the Lackawanna plant of Bethlehem Steel Co., and the Symington-Gould Co. plant at Depew. After the tours, registrants were returned to the Statler, where a luncheon was held, courtesy of the host companies.

As in the past, suppliers amply provided for the after meeting hours of the registrants.

Incoming officers for the Blast Furnace, Coke Oven and Raw Materials Committee are: C. C. Russell, Chairman; W. E. Marshall, Vice-Chairman; Kurt Neustaetter, Vice-Chairman; E. J. Andberg, Secretary; and Ernest Kirkendall, Treasurer. National Open Hearth Steel Committee officers are: L. R. Berner, Chairman; J. J. Golden, Past Chairman; L. A. Lambing, Vice-Chairman; and Ernest Kirkendall, Secretary-Treasurer.

Dan Loughrey, serving as toastmaster, evoked a stream of laughter with his amusing patter at the Fellowship dinner.

Session chairmen and authors of papers met informally at breakfast every morning of the Conference. These "behind the scenes" get togethers gave sessions much of the air of organization and competence which typified the entire conference.

J. V. BEALL

A. S. COHAN

C. M. COOLEY

New Appointments Announced For Institute Publications

John V. Beall, Manager of Publications of AIME and Editor of MINING ENGINEERING, has resigned to accept a position in the Raw Materials Dept. of the Atomic Energy Commission in New York. Mr. Beall had been with the Institute since 1948, starting as Assistant Editor of MINING AND METALLURGY. He became Editor of MINING ENGINEERING in 1949 when that magazine was started, and in 1950 was also appointed Eastern Secretary of the Mining Branch, a position he held until April 1952. He was made an Assistant Secretary of the Institute in 1951. Mr. Beall is a graduate of the School of Mines, Columbia University. He previously held positions at Idaho Maryland Mines, Grass Valley, Calif., and with Howe Sound at Holden, Wash. His new position will involve exploration work for the Atomic Energy Commission.

Alvin S. Cohan has been appointed Acting Manager of Publications to succeed Mr. Beall. Mr. Cohan graduated from Rensselaer Polytechnic Institute as a metallurgical engineer, and did some graduate work at New York University. He started with the Institute as Assistant Editor of JOURNAL OF METALS in 1950, after several years experience in industry. He became Editor of JOURNAL OF METALS in 1952, and will continue as Editor in addition to his new duties.

Charles M. Cooley, Secretary of the Mining Branch and Associate Editor of MINING ENGINEERING, has been appointed Acting Editor of that journal in addition to his Secretarial duties. Mr. Cooley came to the Institute from Climax Molybdenum Co. in 1951, where he was Assistant Chief Engineer. He became Associate Editor of MINING ENGINEERING and in 1952 was appointed Secretary of the Mining Branch. Mr. Cooley, a mining engineer, is a graduate of Texas Western College of the University of Texas at El Paso.

Columbia Section Meets

A program organized and presented by students of the University of Idaho and Washington State College, drew miners, geologists, and metallurgists to Pullman, Wash. Dwight L. Myers, Chairman of the Spokane Section made a brief introduction and Deans Spielman and Fahrenwald gave an explanation of the program.

Before the meeting, the metallurgical and mining facilities for teaching and experimental station were visited.

Conrad Pilz, president of the Washington State College AIME Chapter, and Robert Lathrop, president of the Idaho AIME Chapter, introduced the various speakers.

The Present Lead and Zinc Situation was discussed by William Grave; *Aluminized Iron*, J. R. Miller; and *Factorial Design vs Standard Testing* was the subject of Elwood Gray's talk. Cole McFarland explained the *Sluice Plate Operation in Alaska Gold Placers*. Bruce Wormald spoke on *Idaho Batholist; Spectroscopic Analysis as Applied to a Few Metallurgical Products* was discussed by Elwood Strom; and Clayton Harmsworth presented his subject, *Millesecond Delay Blasting*.

Among those active in the organization of the meeting was Whit Smith.

Nominating Committee Report Is Unanimous

S. S. Clarke, Chairman of the Nominating Committee for AIME Officers in 1954, states that the report of the Committee was made unanimous by mail vote following the meeting of the Committee in Los Angeles in February. The ticket was headed by Henry DeWitt Smith for President-Elect.

F. L. LaQue Speaks At Philadelphia Meeting

F. L. LaQue, International Nickel Co., was speaker at the recent meeting of the AIME Philadelphia Local Section. He spoke on corrosion and emphasized the fact that the comparison of electrical potentials of pairs of metals in a given electrolyte is an inadequate measure of their behavior under actual conditions. The importance of such factors as current density, velocity of the medium, oxygen content, etc. was brought out. Following his talk, a question and answer period followed and Mr. LaQue illustrated his points with examples drawn from his practical experience in this field.

ANNUAL MEETING PAPER DEADLINE

Sept. 15, 1953 is the deadline for all Institute of Metals Div. papers for the 1954 New York Annual Meeting and the deadline for all Iron and Steel Div., and Extractive Metallurgy Div. papers to be prepublished.

Board Approves Four Engineering Projects

Four projects in the field of the AIME have been approved by the Board for financial support by the Engineering Foundation as follows:

1—$10,000 to the Alloys of Iron Research to help defray the cost of preparing and printing a special monograph on *The Principles of the Heat-Treatment of Steel.*

2—$3500 for Project No. 80, *Unsteady Heat Flow Investigations,* by V. Paschkis.

3—$2500 for Project No. 97, *Diffusion in Steel,* by Morris Cohen.

4—$3000 for Project 104, *Comminution,* by A. M. Gaudin.

Any AIME member who wishes financial support of research work, and who can command an equal amount from industrial sources, may apply for a grant from Engineering Foundation.

Chicago Section Holds Students' Night

Representatives from several universities attended the Chicago Section's recent meeting designated as Annual Students' Night, held at the Chicago Bar Assn.

W. H. Zinn, director of Argonne National Laboratories addressed the meeting on *Power Production from Atomic Energy.*

A. Fletcher Addresses San Francisco Section

President Fletcher was the principal speaker at the April meeting of the San Francisco Local Section. He reported on Institute activities and gave an informative analysis of the effect of foreign metal imports on the domestic mining industry today. Legion of Honor Medals were presented to L. A. Levensaler and E. H. Nutter before a group of approximately 80 persons.

A luncheon was given by Chairman J. G. Huseby after which President Fletcher met with D. C. Jackling, a former President of AIME.

AIME Represented In NBS Investigation

Dismissal of Dr. Allen V. Astin, director of the National Bureau of Standards, by Secretary Weeks, of the Dept. of Commerce, two or three months ago aroused a storm of protest from professional men. It appeared that the dismissal was caused by an adverse opinion of the Bureau on a certain additive to storage batteries, which the makers argued was a meritorious product. Most of the professional societies felt that the matter was of a political nature and that they should not sit in judgment. They agreed, however, to participate in a committee named, as Secretary Weeks expressed it, "to evaluate the present functions and operations of the Bureau of Standards in relation to the present national needs." Clyde Williams was named by the AIME as its representative on a seven-man committee headed by Dr. M. J. Kelly, president of the Bell Telephone Laboratories.

Annual Meeting Figures

Final figures for attendance at the Annual Meeting in Los Angeles, Feb. 16 to 19, 1953, were as follows:

Members	1576
Student Associates	78
Nonmembers	301
Students, not SA's	48
Unregistered men	116
Ladies, members WAAIME	336
Ladies, not members WAAIME	155
TOTAL	2610

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Volume 194 1952

Contains the technical papers of the three divisions of the Metals Branch published in the Transactions section of JOURNAL OF METALS. The technical papers and discussions of the Institute of Metals Div., Iron and Steel Div., and Extractive Metallurgy Div. are presented under a single cover in addition to Technical Notes.

MINING BRANCH TRANSACTIONS
Volume 193 1952

Contains the technical papers and discussions published in the Transactions Section of MINING ENGINEERING, covering: Metal Mining, Minerals Beneficiation, Coal, Industrial Minerals, Geology, Mineral Economics and Geophysics.

PETROLEUM BRANCH TRANSACTIONS
Volume 195 1952

Contains all technical papers published in the JOURNAL OF PETROLEUM TECHNOLOGY.

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IMD New England Regional Conference Draws 235 Registrants To Three-Day Session Held at GE Research Laboratory

Seventh Annual Conference

Characterized by Excellent Papers and Lively Discussion With Many Participating at Technical Sessions

The Seventh Annual New England Regional Conference of the Institute of Metals Div., AIME, held at the General Electric Research Laboratory, Schenectady, N. Y., successfully added to the ever-growing reputation of this annual event.

Some 235 registrants flocked to the three-day session to hear and present papers on Deformation, Research in the Schenectady Area, Extrusion, and New Techniques in Metallurgy. At the conclusion of almost every paper listeners took over the floor avidly, discussing, debating, and adding to the information offered.

In addition to the technical success of the conference, the Friday night banquet feature social event wound up activities in grand fashion, with more than 100 persons taking part.

Deformation led off the sessions, with J. C. Fisher of the GE Laboratory presenting a paper on current *Theories of Deformation*. Dr. Fisher concentrated on the success of the dislocation theory in explaining various aspects of the plastic deformation of metals. He also emphasized the limits on current understanding.

Columbia University's T. A. Read offered a paper on *Deformation and Surface Defects*. Dr. Read reviewed the influence of various surrounding media on the mechanical behavior of metals. A. H. Geisler dealt with *Spontaneous Deformation During Transformation*. In addition to summarizing available information on the martensite reaction in ferrous and nonferrous systems, he discussed various crystallographic mechanisms for this reaction.

N. J. Grant, MIT professor, presenting the final paper, spoke on *Deformation at High Temperatures*. His discussion detailed mechanisms of deformation at elevated temperatures and reviewed aspects of high-temperature behavior of metals.

Increased knowledge has not led to isolation of the subject of deformation, rather it has made clearer the connection of the field with other subdivisions of physical metallurgy, according to the closing remarks of MIT professor, M. B. Bever, Session Chairman. He added that plastic deformation is moving closer to the center of metallurgical interest.

During the session on *Research in the Schenectady Area*, registrants displayed considerable interest, developing several discussions from the floor at the conclusion of each paper. The papers presented gave a broad picture of various phases of metallurgical research in the area, leading off with J. H. Hollomon's description of the metallurgical research currently undertaken at the GE laboratory. GE is investigating metals, alloys and ceramics with a view toward high temperature applications. Metallic materials and *ferrites* are under study for electrical applications. Motion pictures on crystal growth around screw dislocations in cadmium iodide and formation of mercury *whiskers* illustrated the nature of GE's fundamental approach toward obtaining materials with near theoretical strength. J. E. Burke outlined research at the GE Atomic Power Laboratory. Mr. Burke offered as examples of metallurgy related to nuclear reactors, studies on the effects of radiation on metals and martensite reaction in uranium.

Rensselaer Polytechnic Institute work on sintered alloys with controlled porosity for sweat cooling, sintered aluminum powder and resistance welding of low alloy steels was offered as examples of that institution's broad program by A. A. Burr, metallurgy professor. J. Van Ullen disclosed some of the problems under consideration at GE's Materials and Processes Laboratory. He discussed testing of alloys for high temperature service and the significance of results with notched and unnotched test specimens, and problems involved in salt bath quenching of a large low alloy steel housing for a steam turbine application. W. H. Sharp, Pratt & Whitney Aircraft, was Chairman.

Three papers were presented on the *Extrusion* program. Donald K. Crampton, director of research and development, Chase Brass & Copper Co., prepared the paper on *Extrusion Principles*, presented by Richard E. Russell, Chase research metallurgist. Mr. Crampton's paper offered the results of recent experiments to evaluate the effects of such variables as metal flow rate, extrusion pressure, and several dimension variables.

Edward S. Bunn, metallurgical manager, magnesium div., Revere Copper & Brass Co., described many of the operating details pertaining to extrusion of aluminum and aluminum alloys. Jerome Strauss, vice-president and technical director, Vanadium Corp. of America spoke on *Glass Lubricated Extrusion*, describing the new development in detail. He described the successful application to metals which could not be extruded by previously known methods. A motion picture of glass lubricated extrusion practice in France was shown. The process originated in that country. A. I. Blank, Chase Brass & Copper Co., held the chair at this session.

J. M. Berry sounded a warning to researchers using thermocouples for precise temperature control. Speaking at the Saturday morning session, Mr. Berry included experimental data in his paper which demonstrated the more familiar sources of error because of aging of chromel-alumel couples could lead to errors of as much as 25°C. C. E. Weber, after reviewing some effects of radiation damage to metals, described techniques for examination of radioactive samples. He noted that increasing radiation intensity requires more remote handling, adding to time needed for experiments.

W. D. Robertson, speaking at this session, recommended more extensive use of electrical measurements. Such techniques can be used for obtaining thermodynamic data with reactions which are reversible and for studying physico-metallurgical phenomena not involving reversible reactions.

The Conference Committee consisted of James H. Moore, National Research Corp., Chairman; Winston H. Sharp, Pratt & Whitney Aircraft, Vice-Chairman; Franklin H. Wilson, American Brass Co., Secretary; Leo P. Tarasov, Norton Co., Treasurer; Albert I. Blank, Chase Brass & Copper, Past Chairman; Michael B. Bever, MIT; Daniel Cushing, consulting engineer; William D. Robertson, Yale University; William L. Stearns, Bridgeport Brass Co.; George P. Swift, consulting engineer; and Leon W. Thelin, Chase Brass & Copper.

F. H. Wilson, assistant research metallurgist, American Brass Co.; A. I. Blank, research metallurgist, Chase Brass & Copper Co.; M. B. Bever, associate professor of metallurgy, MIT; and W. H. Sharp, engineering metallurgist, Pratt & Whitney Aircraft aided in recording events of the conference.

Personals

John S. Dawson, secretary and general counsel of the Bridgeport Brass Co., was named a vice-president.

P. E. Dempsey is forge and melting metallurgist for Sorel Industries, Ltd., Sorel, P. Q., Canada.

J. A. Kavenaugh recently accepted the position of chief process engineer with Rheem Mfg. Co., Downey, Calif. He had been with Revere Copper & Brass, Inc.

Ray L. Farabee was appointed a vice-president of Delta Tank Mfg. Co., Inc., a subsidiary of General Gas Corp.

Horace Y. Bassett was named vice-president of operations, Calumet & Hecla, Inc. **Don W. Blend** succeeds Mr. Bassett as general manager of the Wolverine tube div.

H. C. LEE

Harley C. Lee has been elected a director of Basic Refractories, Inc., Cleveland. Mr. Lee joined Basic in 1926 and has been a vice-president since 1945. He had also been in charge of the technical dept. of Basic Magnesium, Inc., a subsidiary and director of research for Basic Refractories.

Harry V. Joyce is ordnance metallurgist with U. S. Steel Corp., Pittsburgh.

Robert W. Berkhahn has resigned as metallurgist with the M. A. Hanna Co. to accept a position of sales engineer with the Western Mining Co.

John R. McVeigh recently joined the research and development staff of the Alloy Engineering & Casting Co. as chief engineer.

George E. Stone has been named chief engineer for Basic Refractories Inc., Cleveland.

J. H. EISAMAN

Jack H. Eisaman, formerly superintendent No. 4 open hearth, South works, U. S. Steel Corp., has accepted the position of midwest sales representative, International Graphite & Electride div., Speer Carbon Co.

N. S. Spence, formerly sales manager for Dominion Magnesium Ltd., has transferred to the operating div., metallurgical dept.

Charles M. Schwartz was named to supervise a research group engaged in X-ray and electron diffraction, electron and light microscopy studies at Battelle Memorial Institute.

William M. Bausch, formerly sales manager for mill products, has been named assistant vice-president in charge of mill sales for Follansbee Steel Corp.

Donald B. Palmer, Jr., was appointed bituminous sales engineer for Pioneer Engineering Works, Minneapolis.

Charles B. Spencer has been named winner of the Egleston Medal, top honor of Columbia University's Engineering Alumni Assn. The award is presented annually to a Columbia engineering graduate on the basis of outstanding engineering achievement. Mr. Spencer is president of Spencer, White & Prentis, New York.

Lyle L. Clark, C. Robert Lillie, and **Jack Giddens** recently joined the staff of the metals research dept., Armour Research Foundation of Illinois Institute of Technology.

Theodor Wutscher has been appointed chief designer of the rolling mill div., Hydropress, Inc., New York.

George K. Dreher, has joined the Waukesha Foundry Co., Waukesha, Wis., as manager of the casting div. and a director.

W. E. Ackermann, assistant vice-president of the Wheeling Steel Corp., has retired. Mr. Ackermann had also been president of Ackermann Mfg. Co. and vice-president of Wheeling Corrugating Co.

Thomas R. Moore, assistant to vice-president, General Dyestuff Corp., has been elected president of the Metal Powder Assn. **Ernest H. Klein,** manager, metal div., New Jersey Zinc Sales Co., was elected chairman of the board. **Robert L. Ziegfeld** was reelected acting secretary-treasurer. **William E. Cairnes, Thomas L. Robinson,** and **Paul E. Weingart** were elected vice-presidents.

Robert C. Mohr is now employed as sales engineer by John Mohr & Sons, Chicago. He had been associated with the U. S. Steel Corp.

Rowland H. George has been elected a director of the American Metal Co., Ltd. **Thomas W. Childs, Herbert S. Cohen, Hugo de Neufville, Ernest T. Rose, Hans A. Vogelstein,** and **Jean Vuillequez** have been elected vice-presidents.

M. Nielsen who was elected a vice-president of the Babcock & Wilcox Co. has been placed in full charge of the mfg. dept., of the company's boiler div.

L. P. Barrett has retired from the Jones & Laughlin Steel Corp. He is now residing at Ishpeming, Mich.

J. C. HICKS

James C. Hicks has been appointed director of refractory research for Kaiser Aluminum & Chemical Corp., Oakland, Calif. Mr. Hicks has been associated with the development of the company's refractory products for basic industry.

Obituaries

Philip S. Morse (Member 1884) died on March 1 at his home in Brookline, Mass. Mr. Morse was one of the oldest members of the Institute and one of three surviving members of the class of 1881 at Harvard. He received his engineering degree from Massachusetts Institute of Technology in 1884. During his professional career he was employed by the Pueblo Smelting & Refining Co., Pueblo, Colo.; worked in Europe, Mexico, and Australia. He had been connected with the Sulphide Corp. in Australia, the Dwight Lloyd Sintering Corp., New York, and American Smelting & Refining Co. He had retired about 25 years ago.

Edward A. Uehling (Member 1886), born at Richmond, Wis. in June 1849, died on Dec. 21, 1952. Mr. Uehling was a graduate of Stevens Institute of Technology in 1877. During his employment he held positions of chief chemist, superindendent blast furnaces, furnace manager, and was head of the Uehling Instrument Co., which he organized in 1895. Mr. Uehling held more than 20 patents and developed a pyrometer that indicated and recorded temperatures up to 2500°F. Mr. Uehling had experience in England, Germany, and Austria. He was also known for the invention of the pig iron casting machine and made outstanding engineering contributions to the field of instrumentation.

J. Irving Prest (Member 1949), a resident of Waukegan, Ill. has died. Mr. Prest was a graduate of the Armour Institute of Technology (B.S.) 1918. After graduation he was a metallurgical chemist with the Bureau of Mines at the Pittsburgh and Seattle experiment stations. In 1921 he joined the International Harvester Co., Chicago, as metallurgist. For 21 years Mr. Prest was associated with the American Steel & Wire Co., Waukegan. In 1944 he resigned to accept a position with the Outboard Maine & Mfg. Co., Johnson motors div., Waukegan, as chief metallurgist. He held membership in the American Chemical Society, American Institute of Physics, and ASM.

NECROLOGY

Date Elected		Date of Death
1949	Kelber Bordez	Unknown
1916	Hugh Robert Edwards	Feb. 23, 1953
1934	Gerald B. Gould	Mar. 20, 1953
1950	Norman C. Prudent	Unknown
1908	Bertram D. Quarrie	Feb. 15, 1953
1936	Robert C. Ried	Mar. 27, 1953
1905	H. St. J. Somerset	Sept. 20, 1952
1906	M. W. Summerhayes	April 1953

Proposed for Membership

— Metals Branch AIME —

Total AIME membership on Mar. 31, 1953 was 18,475; in addition 1098 Student Associates were enrolled.

ADMISSIONS COMMITTEE

O. B. J. Fraser, Chairman; Philip D. Wilson, Vice-Chairman; F. A. Ayer, A. C. Brinker, R. H. Dickson, Max Gensamer, Ivan A. Given, Fred W. Hanson, T. D. Jones, G. W. Lutjen, E. A. Prentis, Sidney Rolle, J. T. Sherman, F. T. Sisco, R. L. Zieyfeld.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama
Bessemer—Granger, Walter C. (J) (R. C/S—S-J)

California
Hermosa Beach—Harsell, Thomas L., Jr. (M)
Los Angeles—Jepson, James O. (J) (R. C/S—S-J)
Oakland—Scott, W. Kenneth (M)
San Francisco—Caldwell, Robert C. (M) (R. C/S—A-M)
Whittier—Cubicciotti, Daniel D. (M)

Colorado
Leadville—Burton, Robert S. (M) (R. C/S—J-M)

Georgia
Tate—Durrett, Thomas J., Jr. (M) (R. M)

Illinois
Caseyville—Tschirner, Henry J. (M) (C/S—A-M)
Chicago—Gray, Robert A. (M)
Chicago—Hammer, Rudolph G. (M)
Chicago—Hiler, Robert J. (M) (C/S—A-M)
Chicago—Johnson, C. Philip (M)
Homewood—Hawkinson, Marshall J. (M)
Homewood—Wallace, John W. (M)
Lake Bluff—Sutherland, Earl C. (J)

Indiana
Chesterton—Stokes, Chester H. (M)
Gary—Stephan, Raymond C. (M)

Massachusetts
Boston—Chang, Hsing C. (A) (R. C/S—S-A)

Michigan
Calumet—Bastian, Clarence J. (M)
Detroit—Reich, William A. (M) (R. C/S—S-M)
Detroit—Tache, Arthur J. (J) (C/S—S-J)

Montana
Butte—Hawkesworth, Maurice W. (M)
Great Falls—Ingvalson, Lawrence J. (J) (R. C/S—S-J)

Nevada
Boulder City—Petermann, Fernando B. (M)

New Jersey
Keyport—Putman, John W. (J) (C/S—S-J)
Perth Amboy—Barrett, Kenneth R. (J)
Radburn—Counselman, Edward G. (M) (R. M)

New York
New York—McCullough, James D. (M)
Utica—Lupi, Richard F. (J)

Ohio
Oak Harbor—Rader, Jack E. (M)
Owensville—Leininger, James V. (A)
Steubenville—Holman, William H. (M)
Steubenville—Snyder, Ernest B. (M)
Steubenville—Strassburger, Julius H. (M)

Pennsylvania
Latrobe—Robb, Frank M. (A)
McKeesport—Ely, John P. (A)
Philadelphia—Taylor, Paul E., Jr. (J) (C/S—S-J)
Pittsburgh—Randig, Robert T. (J) (R. C/S—S-J)
Ridley Park—Hersch, Joseph E. (M) (C/S—A-M)
Springfield—Corriston, John W. (M)
State College—Osborn, Elburt F. (M)

Washington
Liberty Lake—Mateer, Richard S. (J)

West Virginia
Weirton—Carr, Charles E. (M)

Canada
B. C., Trail—Turner, Gordon H. (M)
Ontario, Port Colborne—Crichton, James T. (M)
P. Q., St. Joseph de Sorel—Martiquet, Jean E. (J)
P. Q., Montreal—Woodhouse, Gordon H., Jr. (M)

England
London—Ruddle, Ronald W. (M) (C/S—A-M)

New Zealand
Wellington—Haqchaudhri, Ihsan-Ul (J)

Coming Events

June 3-7, Chemical Institute of Canada, Windsor, Ont.

June 7-12, SAE, summer meeting, Ambassador and Ritz-Carlton Hotels, Atlantic City, N. J.

June 15-19, Basic Materials for Industry, conference, Hotel Roosevelt; exhibition, Grand Central Palace, New York.

June 16-19, American Welding Society, Shamrock Hotel, Hall of Exhibits, Houston.

June 16-Sept. 4, Gordon Research Conferences, AAAS, New Hampton School, New Hampton, N. H.

June 20-25, American Institute of Chemical Engineers, University of Michigan, Ann Arbor, Mich.

June 29-July 3, ASTM, annual meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.

July 21-28, International Union of Crystallography, general assembly and international congress, Paris.

Sept. 11, AIME, St. Louis Local Section, Lead Belt Meeting, tour St. Joseph mines and mills.

Sep. 13-16, Electrochemical Chemical Society, Inc., Ocean Terrace Hotel, Wrightsville Beach, N. C.

Sept. 21-23, American Mining Congress, Metal and Nonmetallic Mineral Mining Convention, Olympic Hotel, Seattle.

Oct. 7-9, National Assn. of Consulting Engineers, south central region, Mayo Hotel, Tulsa, Okla.

Oct. 8-9, National Conference on Industrial Hydraulics, annual meeting, Hotel Sheraton, Chicago.

Oct. 9, AIME, St. Louis Local Section, St. Louis University, St. Louis, Mo.

Oct. 9, AIME, National Open Hearth Steel Committee, Eastern Section, fall meeting, Warwick Hotel, Philadelphia.

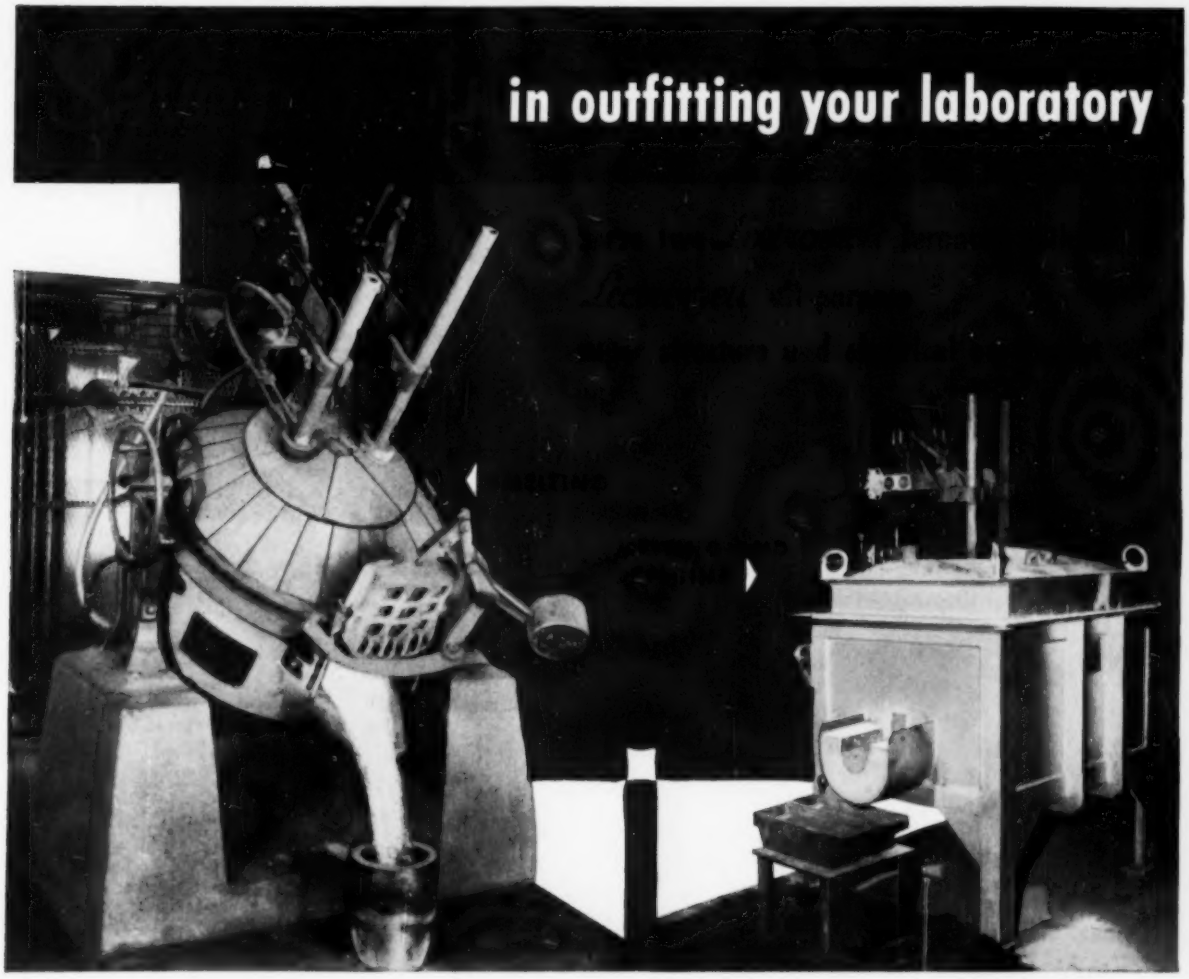
Oct. 15, AIME, National Open Hearth Steel Committee, Southwestern Section, fall meeting, Baker Hotel, Dallas, Texas.

Oct. 19-21, AIME, Institute of Metals Div., fall meeting, Hotel Allerton, Cleveland.

Oct. 19-23, National Metal Congress and Exhibition, Cleveland.

Oct. 27, Assn. of Consulting Chemists & Chemical Engineers, 25th anniversary annual meeting, Hotel Belmont Plaza, New York.

Oct. 28-31, AIME, El Paso Fall meeting, El Paso.



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